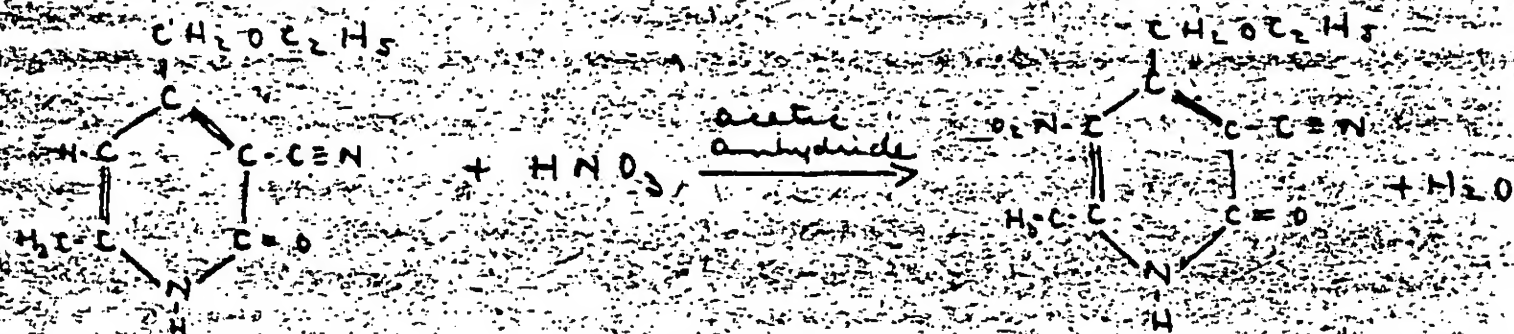


3-Cyano-4-Ethoxymethyl-5-Nitro-6-Methyl-2-Pyridone

1. Reaction



3-Cyano-4-Ethoxymethyl-
6-Methyl-2-Pyridone

3-Cyano-4-Ethoxymethyl-
5-Nitro-6-Methyl-2-Pyridone

2. Reagents

3-Cyano-4-Ethoxymethyl-6-Methyl-2-Pyridone
Nitric acid (Fuming)

3. Reagents

None

4. Yield

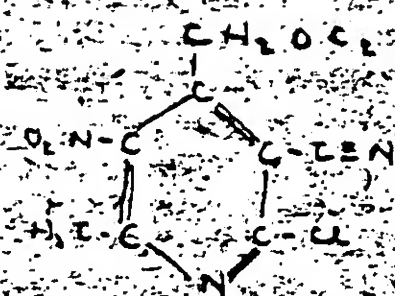
32.7%

5. Unit operations

AN - D₂ - C₄ - I₁ - J₁ - L₃ - N₃ - P₁₀

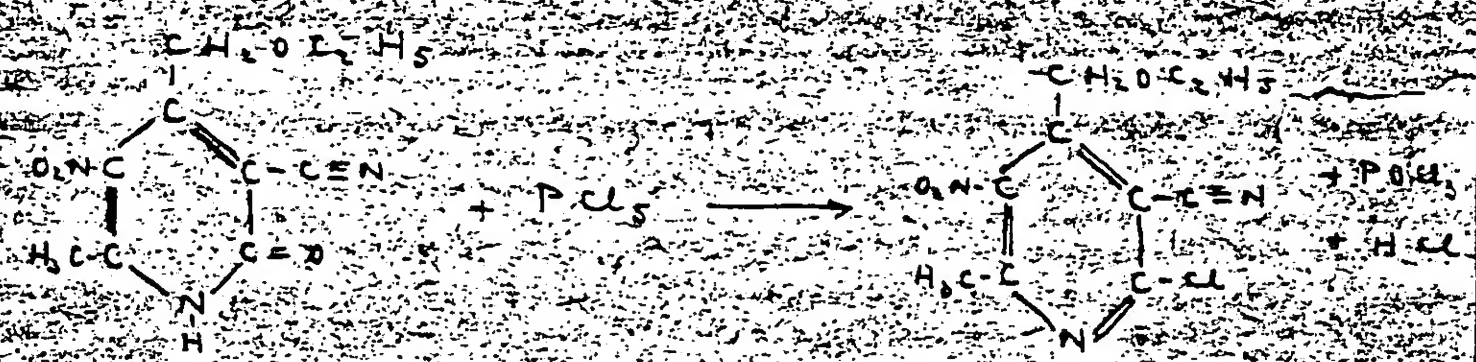
6. Solvents

acetic acid
acetic anhydride
Hydrochloric acid (36.7%)
petroleum ether



5-Cyano-4-Chloromethyl-5-Nitro-6-Methyl-2-Pyridone

1. Reaction



5-Cyano-4-Chloromethyl-5-Nitro-6-Methyl-2-Pyridone

5-Cyano-4-Chloromethyl-5-Nitro-6-Methyl-2-Pyridone

2. Reagents

5-Cyano-4-Chloromethyl-5-Nitro-6-Methyl-2-Pyridone
Phosphorus Pentachloride

3. Results

None

4. Yield

41.7%

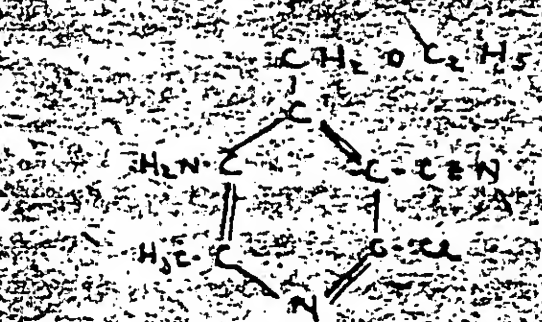
5. Unit operations

A₁₅ - B₂ - C₇ - D₁ - E₁ - H₁ - J₉ - L₄ - N₄ - P₁₀

6. Solvents

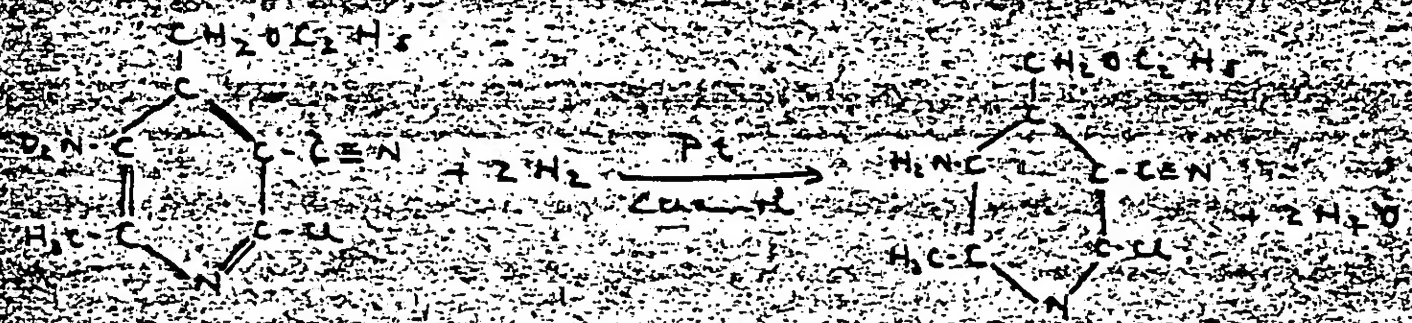
Chlorobenzene
Ethyl alcohol (95%)
Petroleum Ether

Step 6



3-Cyano-4-ethoxymethyl-5-amino-6-methyl-2-chlor-pyridine

Reaction



3-Cyano-4-ethoxymethyl-5-amino-6-methyl-2-chlor-pyridine

3-Cyano-4-ethoxymethyl-5-amino-6-methyl-2-chlor-pyridine

Reactants

3-Cyano-4-ethoxymethyl-5-amino-6-methyl-2-chlor-pyridine

Hydrogen

Reagents

Platinum (Catalyst)

Yield

76.9%

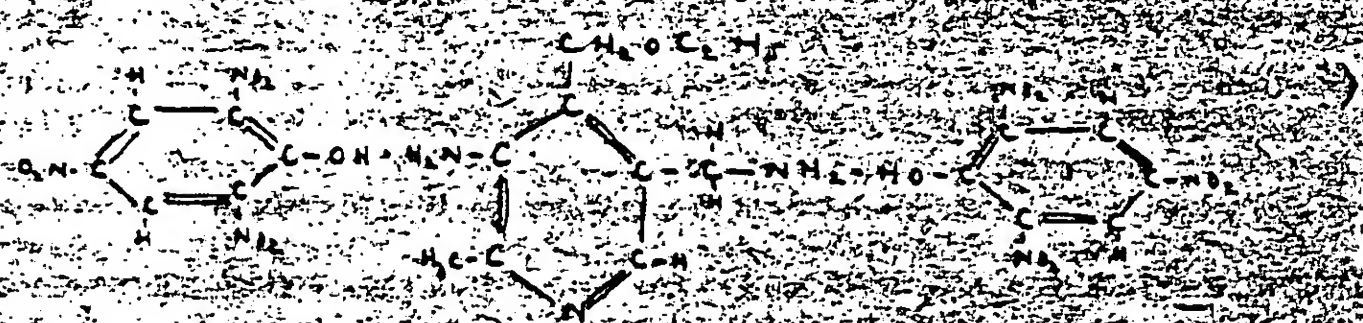
Unit operations

A₁ - D₁ - C₁ - D₂ - E₁ - G₁ - I₁ - J₁ - L₁ - N₁ - P₁

Solvents

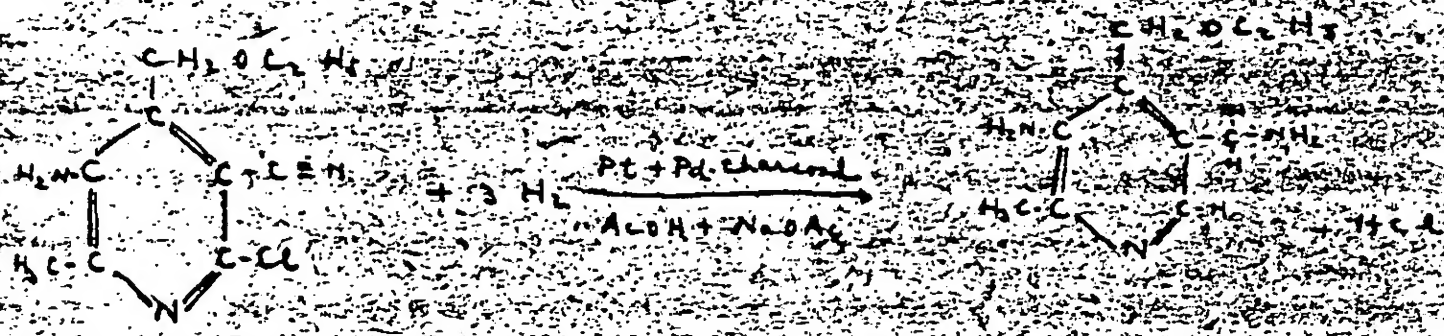
Chloroacetal (95%)

Step 7



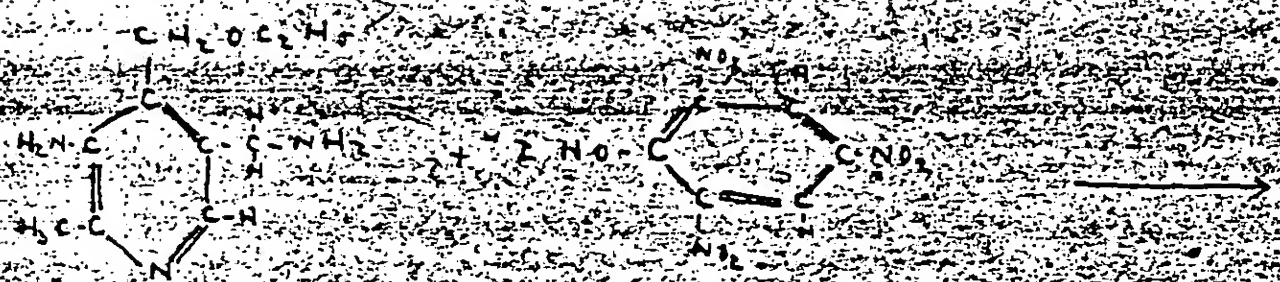
3-Amino-4-ethoxymethyl-5-amino-6-methyl-pyridine-dipicrate

1. Reaction

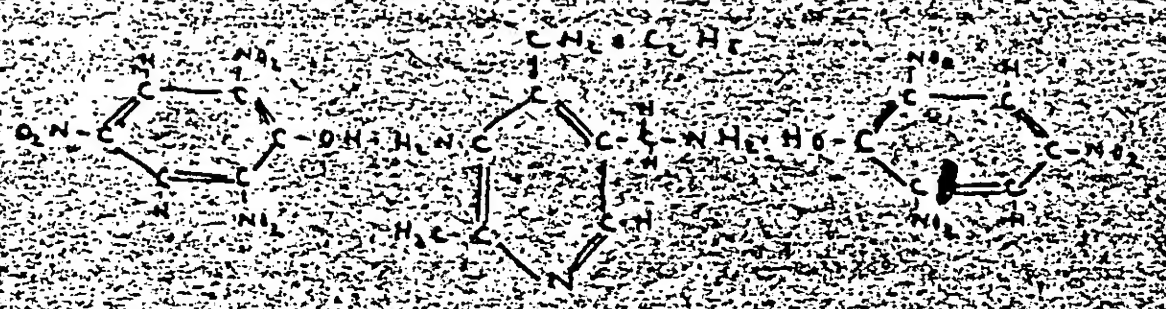


3-amino-4-ethoxymethyl-5-chloro-6-methyl-pyridine + 3 H₂ → 3-amino-4-ethoxymethyl-5-amino-6-methyl-pyridine + HCl

and,



picric acid



3-amino-4-ethoxymethyl-5-amino-6-methyl-pyridine-dipicrate

2. Reagents

3-Cyan-4-ethoxyethyl-5-oxo-6-methyl-2-ethyl-pyridine
Hydrogen
acetic acid

3. Reagents

Pd (catalyst)
Pd-chloride (catalyst)
sodium acetate

4. Yield

55.90

5. Unit operations

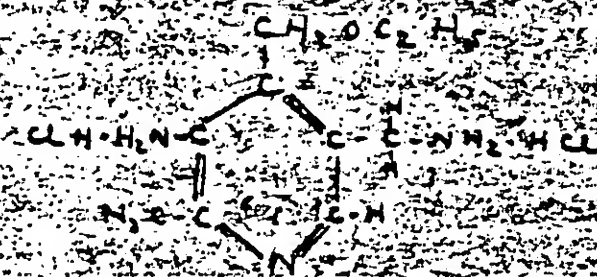
A₆ - D₅ - C₁ - D₂ - G₁ - I₁ - J₅ - L₄ - N₄ - P₁₀

6. Solvents

acetic acid
ethyl alcohol (95%)

Step 7

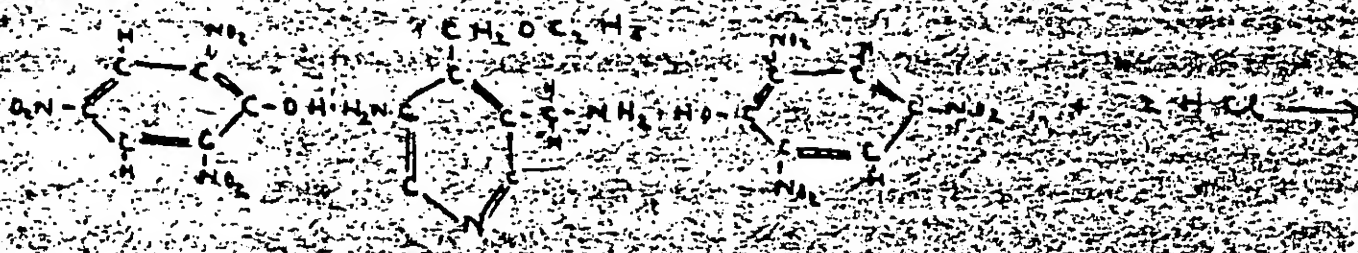
26



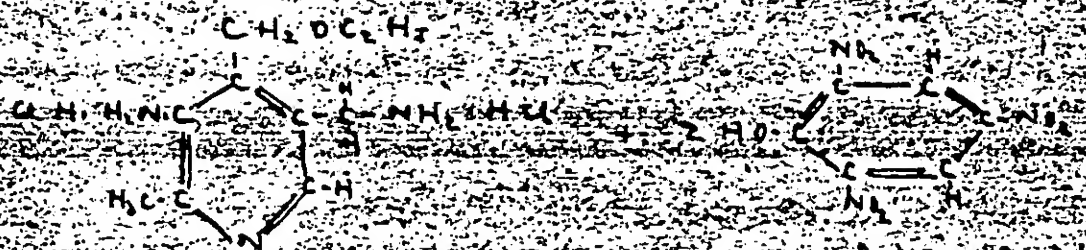
3-aminoethyl-4-carboxyethyl-5-amino-6-methyl-pyridine

hydrochloride

1. Reaction



3-aminoethyl-4-carboxyethyl-5-amino-6-methyl-pyridine Diphosphate



3-aminoethyl-4-carboxyethyl-5-amino

6-methyl-pyridine Diphosphate

2. Reagents

3-aminoethyl-4-carboxyethyl-5-amino-6-methyl-pyridine Diphosphate
Hydrochloric acid

3. Reagents

None

4. Yield

76.70

5. Unit operation

A10-D1-C4-D2-E2-F1-J1-L2-N2-P15

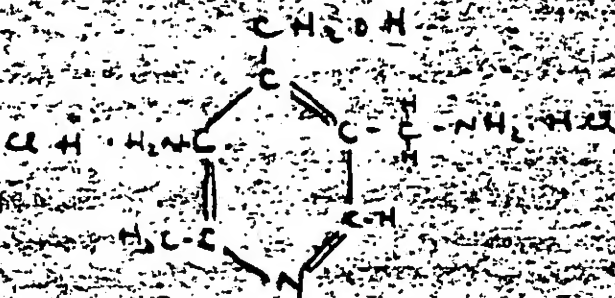
6. Solvents

Nitrobenzene
Chloroform

acetone
ethyl alcohol (anhydrous)

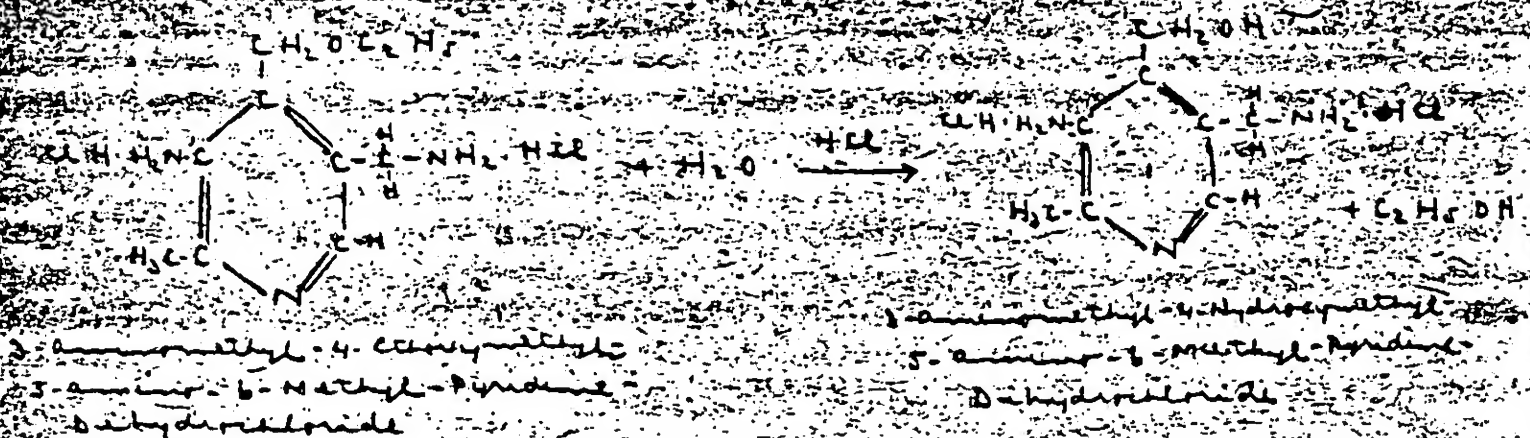
Step 9

D₃



3-aminoethyl-4-hydroxyethyl-5-amino-6-methyl-pyridine
dihydrochloride

Reaction



Reactants

3-aminoethyl-4-hydroxyethyl-5-amino-6-methyl-pyridine
dihydrochloride

Reagents

Hydrochloric acid (2.5 N)
activated carbon

Yield

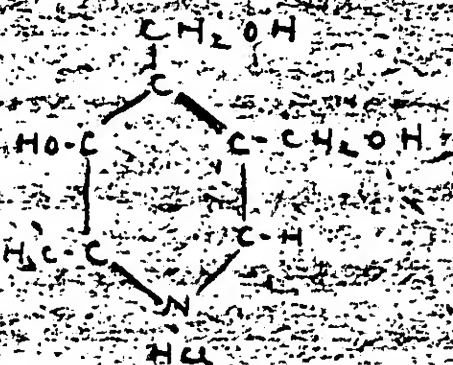
77.70

Unit operations

A₄ - D₂ - C₂ - D₂ - I₁ - J₅ - L₂ - N₁ - P₅

Solvents

ethyl alcohol (31.70)

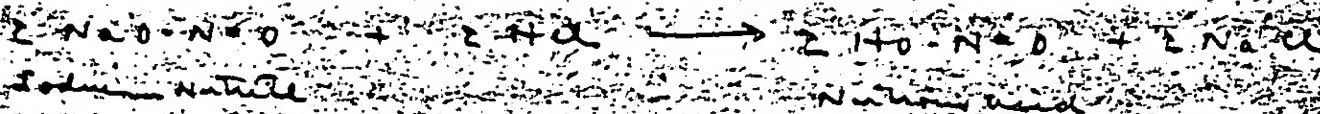


Peridone Hydrochloride

۴۰۰

2,4-Dihydroxy-5-methyl-6-pyridyl-methyl-pyridine

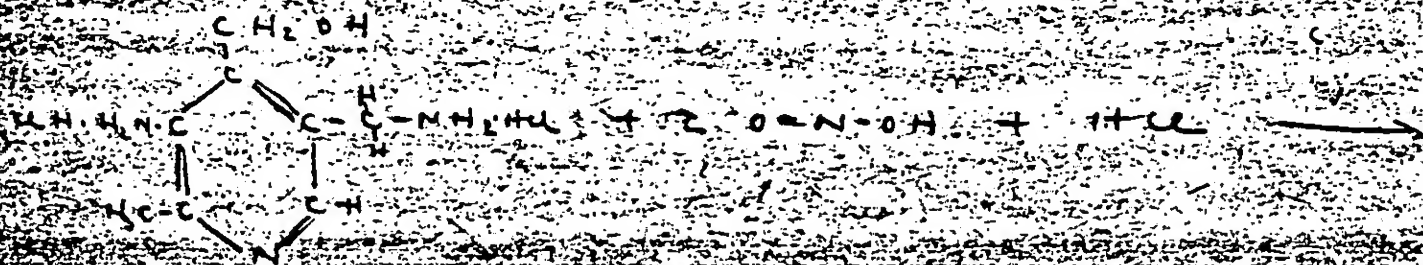
Reaction



John N. H. H.

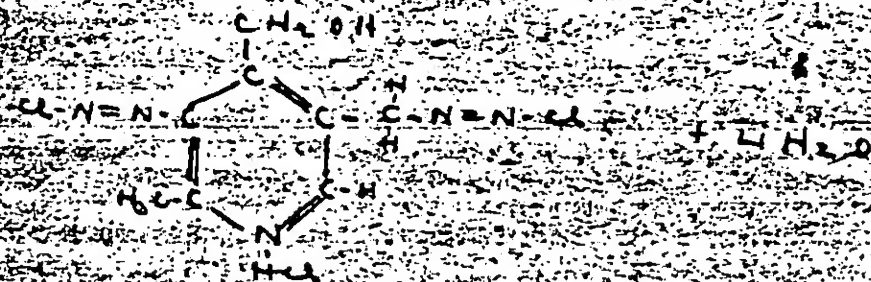
2-11-1944

○



dimethyl-4-4'-dimethyl

بسم الله الرحمن الرحيم

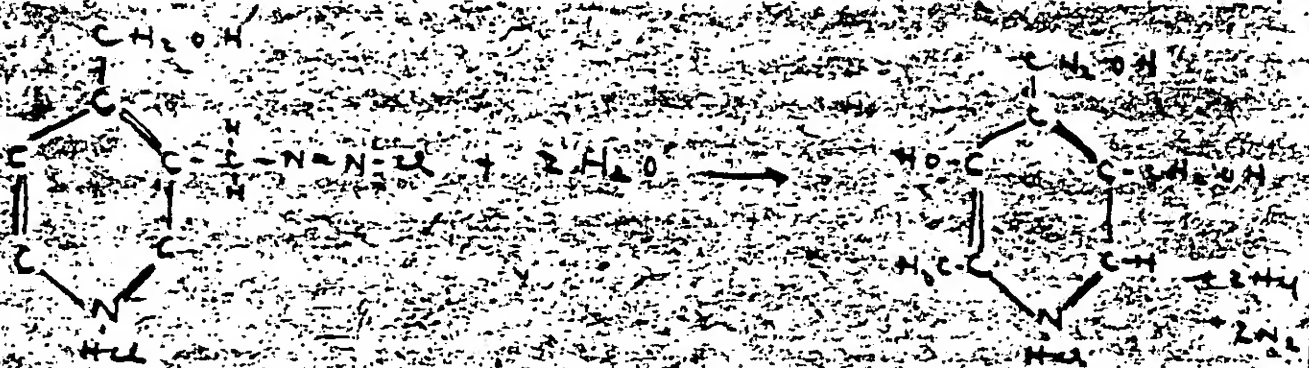


ammodiuron chloride - 4-Hydroxyethyl

5 - Diagonally Cleaved - 6 - Metal - Pyridine

Step 13 (Cont'd)

finally,



3,4-Dihydro-2-methyl-5-hydroxy-6-methyl-2H-pyridine-1,4-dione

2. Reagents

aminoethyl-4-Hydroxyethyl-5-amino-6-methyl-2H-pyridine-1,4-dione
hydrochloric acid
water

3. Reagents

Sodium Nitrate
Hydrochloric acid

4. Yield

4.5 g.

5. Unit operations

A₁₀ - D₃ - C₃ - D₂ - E₁ - I₁ - J₁₀ - L₂ - N₁ - P₁₀

6. Comments

aqueous
ethyl alcohol (anhydrous)

Page 1

Page 2

Page 3

A IIII IIII

B III

C III

D III

E III

F III

G III

H IIII IIII

I III

J III

K IIII IIII

A IIII IIII

B III

C III

D III

E III

F IIII IIII

G III

H III

I IIII IIII

A IIII IIII

B III

C IIII IIII

D III

E III

F III

G IIII IIII

H III

I IIII IIII

GA	GP	GP	GP
A III	A III	A III	A III
B III	B III	B III	B III
C III	C III	C III	C III
D III	D III	D III	D III
E III	E III	E III	E III
F III	F III	F III	F III
G III	G III	G III	G III
H III	H III	H III	H III
I III	I III	I III	I III
J III	J III	J III	J III
K III	K III	K III	K III
L III	L III	L III	L III
M III	M III	M III	M III
N III	N III	N III	N III
O III	O III	O III	O III
P III	P III	P III	P III
Q III	Q III	Q III	Q III
R III	R III	R III	R III
S III	S III	S III	S III
T III	T III	T III	T III
U III	U III	U III	U III
V III	V III	V III	V III
W III	W III	W III	W III
X III	X III	X III	X III
Y III	Y III	Y III	Y III
Z III	Z III	Z III	Z III

<u>Substances</u>			<u>Weight</u>	
acetic acid	273.14	(257.20)		
ethyl alcohol (anhydrous)	243.60			
Iodine	142.32			
HCl (10%)	273.54	(257.20)		
HCl (gas)	56.48			
Na ₂ CO ₃	104.26	(119.30)		
NH ₃ (aqueous, 25%)	36.52	(44.10)		
acetic acid (glacial)	120.60			
HNO ₃ (Fuming)	42.55			
acetic anhydride	293.7			
Urea	23.8			
Piperidine	4.71			
CuSO ₄	155.00 155.8			
Sodium acetate	276			
Pt catalyst	0.37			
Pd (5%) - charcoal catalyst	7.5			
Hydrogen	0.45			
PICRIC ACID	281.8	1.77		
PuS	4.54			
NaNO ₂	0.35			
activated carbon	34.54			
PICRIC ACID				
NaCN				

2400 2.59 27-11-11

2550 (0.43) 2.59 27-11-11

2550 2.59 27-11-11

2550 2.59 27-11-11

2550 (0.71) 2.59 27-11-11

2550 2.59 27-11-11

2550 2.59 27-11-11

2550 2.59 27-11-11

2550 2.59 27-11-11

2550 2.59 27-11-11

$\sqrt{4.6} \times 12.07 = 7.53$ * 3-aminophenol

$\sqrt{4.6 \times (0.55)}$

$\frac{11.5}{31} = 7.59$ * 3-aminophenol

$\frac{0.5}{31} = 7.59$ * 3-aminophenol

$\frac{0.5}{31} = 7.59$ * 3-aminophenol

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$\frac{0.5}{31} = 7.59$ * 3-aminophenol

$\frac{0.5}{31} = 7.59$ * 3-aminophenol

3-aminophenol \rightarrow 3-aminophenol * Step 6

$\sqrt{4.6} \times 12.07 = 7.53$ * 3-aminophenol

$\sqrt{4.6 \times (0.76)}$

$\frac{0.5}{31} = 7.59$ * 3-aminophenol

$\frac{0.5}{31} = 7.59$ * 3-aminophenol

$\frac{0.5}{31} = 7.59$ * 3-aminophenol

$\frac{0.5}{31} = 7.59$ * 3-aminophenol

piperidine \rightarrow piperidine * Step 4

$\sqrt{4.6} \times 12.07 = 7.53$ * piperidine

$\sqrt{4.6 \times (0.41)}$

$\frac{0.5}{31} = 7.59$ * piperidine

$\frac{0.5}{31} = 7.59$ * piperidine

$\frac{0.5}{31} = 7.59$ * piperidine

$\frac{0.5}{31} = 7.59$ * piperidine

$\frac{0.5}{31} = 7.59$ * piperidine

1911

257.1 (0.12) 25.60 64.40
13.7 64.40 176.40
2.2 64.40 23.23
0.2 64.40 2.52

144.1 64.40 60.00
191.7 (0.1) 60.00 47.1
7.3 60.00 47.1
95.1 60.00 47.1

148.1 60.00 192.80
144.1 (125) 192.80 64.05
27 192.80 36.52
25 192.80 36.52
135 192.80 36.52
60 192.80 36.52
149.3 192.80 36.52
141.8 192.80 36.52

94.2 219.30 219.40

138.1 (0.36) 219.40

1250.0791 219.40 220.00 ECH (m)

142 219.40 106.70

69 219.40

142 219.40 220.60 ECH (m)

130.0791 219.40 220.60 ECH (m)

142 219.40 216.90

149.449 219.40 216.90

142 219.40

230.0791 219.40 231.10 ECH

102 219.40

26.4 219.40 26.40

142 219.40

55.11 26.40 90.50

26.4 26.40

92.2 219.40 219.60

94.2 219.40 219.60

142 219.40

142 219.40

142 219.40

144.4 (0.37) 219.40 219.60

142 219.40 219.60

142 219.40 219.60

142 219.40 219.60

142 219.40 219.60

142 219.40 219.60

142 219.40 219.60

142 219.40 219.60

1000 229.70 = 24.4 = 2.4

624 229.70 = 814.5 = 4.4

46750

1200 1200

1200 1200

1200 1200

1200 1200

1200 1200

154.1

154.1

154.1

154.1

154.1

154.1

154.1

154.1

154.1

154.1

154.1



14

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178g. KOH 82 10

500cc. benzene

73-75 CaCl_2

12

16.5g. KOH

35.5-1004

$\frac{75}{12} = 6.5$

13g. CaCl_2

58g. acetone

425cc. methylal

300g. ice.

133

500

84.2

Kennel

#15

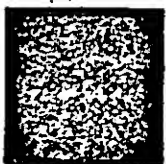
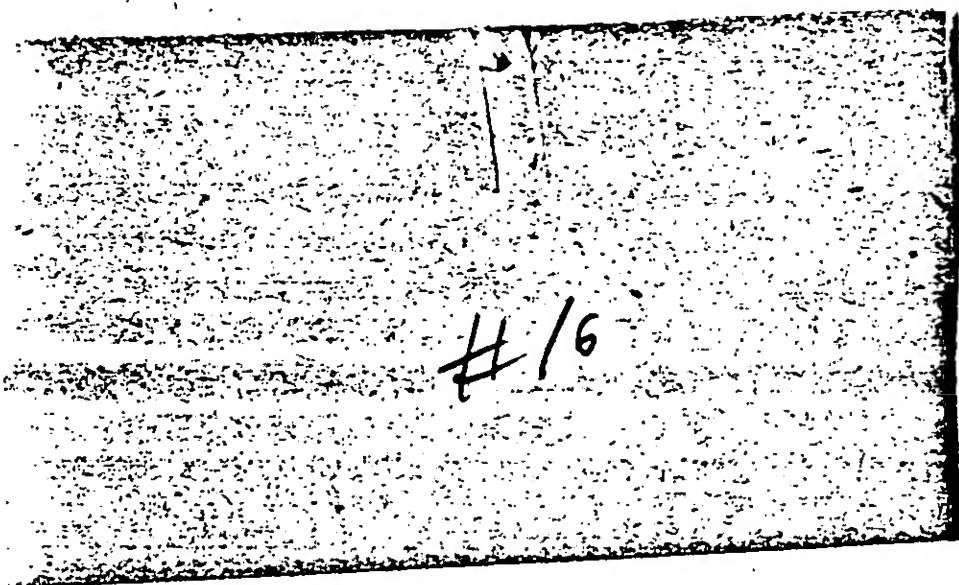
$$X_n = 28 \left(\frac{137 \cdot 265 \times 530}{265 \times 530 + 25} \right)$$

$$28 \left(\frac{196}{221} \right)$$

$$28(1.89)$$

$$\begin{array}{r} 28 \\ 17.6 \\ \hline 16.4 \end{array}$$

$$\begin{array}{r} 2 \times 1 \\ 9.15 - 10 \\ 2960 - 80 \\ \hline 1.60 \end{array}$$



1000 - 200g / 24hrs 32
 1000 / 1/2 lb 0.4
 480,000 14.2 7.1 1.0 12.8 25.6
 6.4 3.2 4

34.4g = 0.2 mole lactide

7.1g = 0.05 mole P₂O₅

2.7g = 0.15 " H₂O

38.4g = 1.2 mole MeOH

40g 50cc

Distilled of C₆H₆

I 80-100

II 110-125

III 135

8g residue

R+H MeOH: butyrate

N₂ 1.4100

1.4110
28
1.4112

Time	Pot Temp	Reflux T
2:15	71°	63
2:45	75° (H ₂ O initial)	63.5
2:50 took 10cc	80°	64°
2:53 took 20cc	87°	64°
3:00 " 1125cc	92°	64°
3:20	92°	64°
3:25 " 30cc	105°	64°
4:00	104°	63.8
4:15 took off 35cc	125°	64°
4:50	125°	63.7
5:50	125.5	63.2
6:45 PM	130	62.4
7:20	135	61.3

2. att. 21.0075
 3/17/47
 2.6g neutralized
 8.3g. H₂O approx.
 Distilled small amt
 material at ca. 130°/20mm
 into 140-180°; Cryst'd
 in condenser

Please let this reflux

overnight, Harry A

11 AM 133° + 8-2 Phil
 1000

236 g (2 mole) - OH ester

42 g (0.62 mole) H_2PO_3

80 cc C_6H_6 + 20 in trap on top of column

OH ester clouded on adding C_6H_6

4 cc H_2O distilled readily with C_6H_6 (pot temp 870)

Then no more H_2O but material which floated on top of C_6H_6

Replaced trap by still head & distilled over night 80 cc C_6H_6 layer + ca 30 cc other mat. (pot temp 90-150°) Material came over a low boiling azeotrope.

Cont'd dist'n with still pot temp remaining at 150° during most of dist'n, finally rising to 170°.

Some polymer formed in column. Temp of vapor varied from 60-95° depending on reflux rate. High reflux ratio gave lowest temp. Collected ca 130 cc distillate which reduced $KMnO_4$ & partially immiscible with H_2O .

The 130 cc was diluted with 40 cc H_2O before clouding. Added total 60 cc H_2O with no sep'n only cloudy. Added 80 cc pet ether with poor sep'n. Sol'n 2 g salt gave good sep'n. Exp'd H_2O layer with 20 cc add'n pet ether. Total pet ether sol'n washed with salt sol'n. Some salt ppted.

44 Ag, phac distilled → 27 g, b.p. 55-6 mm, 1.3590 (n_D acetone 1.3589)

4/21/48

120g. OH ester heated with 115g. NH_4HCO_3 with
stirring - columns. Pot temp 140-5 for most of effst
Rise to 170-5° at end. Distillate 60-105
Depending on rate of takeoff, 0/95 cc. distillate,
all effst but 10-15 cc. (b.p. 76°) was clear at last
few cc. 5-phase. 84g. distillate. Loss in weight
of still pot 101g. Total time ca 7 hrs.

Distillate fairly cloudy on del. in air 50 cc.
H₂O. Added 25 cc. pet. ether & sep'd.

Dist. in aq. layer →

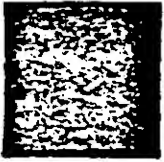
1.6g. b.p. 56-60°

16.8g.

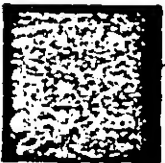
60-65°

(Some H₂O in oil -
probably nitrates)

Small amt. polymer formed in still pot
soon after dist. began. Aq. residue strongly
acid (cat. pH 4). Requiring 22 cc. 0.3054N NaOH
to neutralize to phenolphthalein.



#17



Passed in. Cu^{2+} \rightarrow rise from 20° - 30°
 & holding at 135° for 1 hr.

added acetone 100 gms. @ 15°C some
 slight steady rise obtained. Heated for 5 hrs.
 at 13-15°C.

Decomposed at 2°C with 150 cc H_2O .

Separated two layers - bottom (H_2O) only
 100 cc. added solid $\text{CO}_2 \rightarrow$ Ant. (of K_2CO_3)

Extracted A-M-H (washing ml twice with A-M-H)

Washed A-M-H soln. once with H_2O (equal vol.)
 adjusted pH to 6.0

Distillation

pot.	lower col.	upper col.	temp. - $^{\circ}\text{C}$	Notes
35	—	—	50	
40	35	—	50	
50	40	—	50	distillate 70 cc (occ. H_2O)
Worked over twice - badly (could not get)				
(over) 51	40	31	50	
72	64	63	50	
72	64	63	50	155 cc A-M-H pH 6.9 adj. 6.6
74	66	65	50	
74	63	66	50	pH 6.9 adj. 6.6
75	63	67	50	
76	70	63	50	pH 6.7 adj. 6.2

see
09/9/9

0.328

$$0.164(80) = 13.12$$

Page 245
355.8 mm (am H)

660
4215

Distillation Record

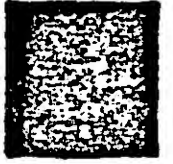
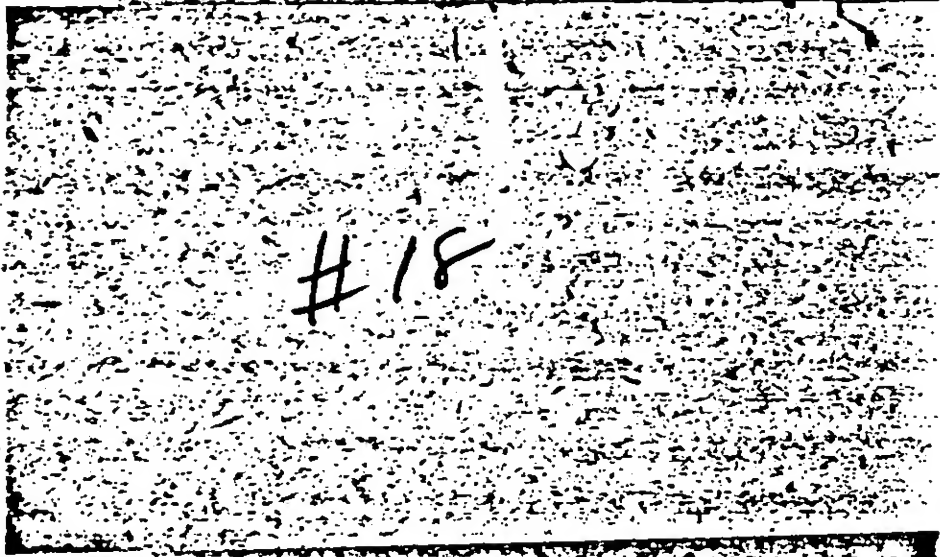
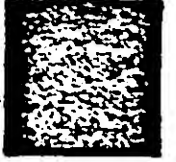
Temp	Loc.	V	Uranic
167	128	90	60-71-75-78
167	129	92	- 80
169	129	94	
173	131	93	- K014 m. t. m.
176	131	92	
178	131	94	
180	133	103	
186	134	120	

reflux 822 11⁰⁰ - 2 1/2 hrs.

add acetone 11⁰⁰

distilled 11⁰⁰ 2 ⁰⁰/_{AM} - 1 1/2 hrs.
-150 come back

102.4
54.1
48.3
10.0
38.3
0.815



Arthur H. Thomas (2)

HR-108 Rubber Stoppers

8808 - Twohole with 2 uniform, funnel top openings

1 doz.	# 00	\$0.29
1 "	0	.33
1 "	1	.37
1 "	2	.39
1 "	3	.45
1 "	4	.48
1 "	5	.54
1 "	5½	.57
1 "	6	.62
1 "	6½	.67
1 "	7	.79
1 "	8	.90

9766 - Tygon tubing, Tygon S22-1

1 carton - 10 ft 3/16" bore \$0.18/ft less 10%

1 carton - 50 ft 1/4" bore \$0.22/ft less 15%

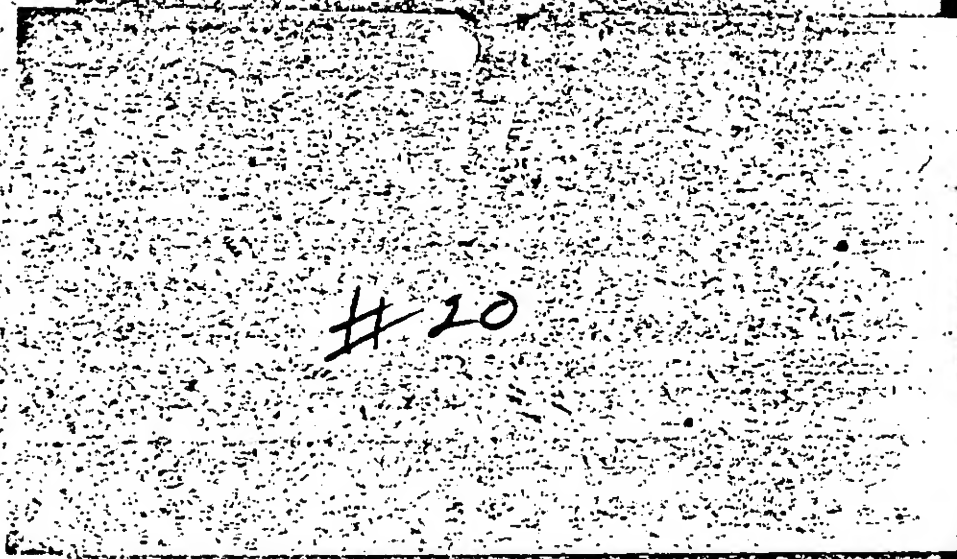
#19

Continuation sheet 5

B₁ (Thiamin) was assayed for by the yeast-growth method of Schultz, Atkin and Frey.

- b. Considerable work was done on the development of special cultures suitable for increasing the Riboflavin, Niacin and Pantothenic acid content of the recovered by-product yeast. This research was successful and resulted in feed values 200 to 300% in excess of what they had previously been.
- c. Some original investigations were completed on assay methods for Biotin and Folic acid as present in feed yeast; these factors of the B complex had then only recently been discovered.

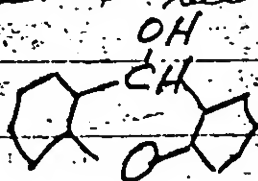
1. Period April 1943 to February 1946



R. Fosse

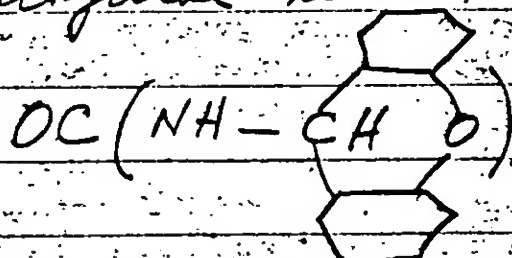
C. - 1914 158, 1076, 188, 159, 210
E.O. I 476

In the presence of a little acetic acid urea
combines with Xanthidrol



to give the very stable

dixanthidrol-urea



which is completely insoluble in acetic acid
water, and cold alcohol. The estimation
is by weighing the precipitate, or a
volumetric modification devised by J. H. Allen
and J. M. Luck (*J. Biol. Chem.*, 1929 82, 693)

Organic Chemistry of Nitrogen

POD

Taylor + Baker

pp. 280-

Oxford 1937

21

TRANSLATION FROM THE FRENCH

Mode of operation A

The solution of urea is increased first with 35 times its volume of acetic acid, then with its half volume of alcoholic xanthidrol.

After one hour the white boiled mixture, crystallized, is dried in the air, washed in alcohol, dried, weighed and analysed.

Titer in urea(1)

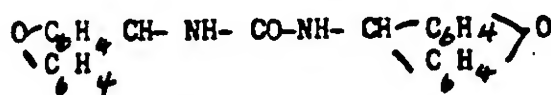
Theory	found →
5 g	4.93 g 4.955 4.934
2 g	2.04
1	1.0085 1.011

If one compares the results of the analysis with the solution of urea in the amount of 5 grammes with those of less concentrated liquids which follow, one notes that the mistake made changes its indications. While it is defective and fluctuates around -1 per cent for the titer of 5 grammes, it rises to +2 per cent for the liquid in the amount of 2 grammes. The explanation of this fact, which may seem quite remarkable a priori, is given us by the analysis. The latter establishes that the percentage in nitrogen of urine decreases slightly and hence its purity also when the proportion of the xanthidrol to urea increases in the reactionary mixture.

Z. Lyon

TRANSLATION FROM THE FRENCH

These results, due to the xanthidrol, spring from the formation of a definite compound, crystalized, very little soluble and seven times higher in molecular weight than that of urea:



Xanthidrol is just as valuable for the quantitative analysis of urea. The new method which is based on its use differs essentially from those which are in usage by its principle and the control to which it admits.

Instead of destroying the carbamide and restoring its proportioning to the measure of its products of decomposition, we convert it almost quantitatively into its characteristic dixanthin derivat which we weigh.

Composition of the medium used for the proportioning of urea

Titrated solution of urea	1 cm	20 cm
Crystallizable acetic acid	3.5	70
Xanthidrol liquid in the amount of 1/10 in pure alcohol	.5	10
	<u>5.0</u>	<u>100</u>

s.l.gon

Mode opératoire A

La solution d'urée est additionnée d'abord de 3.5 fois son volume d'acide acétique, puis de son demi-volume de l'anthracol alcoolique.

Après 1 heure, la bouillie blanche, cristalline, est essorée, lavée à l'alcool, séchée, pesée et analysée.

Titre en urée (l.)

Théorie trouvée

5g	4.939
	4.955
	4.924

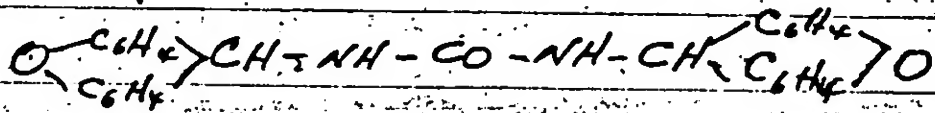
2g	2.04
----	------

2

1	1.0085
	1.011

Si l'on compare les résultats du titrage de la solution d'urée à 5g avec ceux des liqueurs moins concentrées qui suivent, on constate que l'erreur commise change de signe. Tandis qu'elle est déficitaire et oscille autour de -1 pour 100 pour 5g, elle s'élève à +2 pour

Ces résultats, du sur Xanthydrol, découlent de la formation d'un composé form défini, cristallisé, fort peu soluble et de poids moléculaire sept fois plus élevé que celui de l'urée:



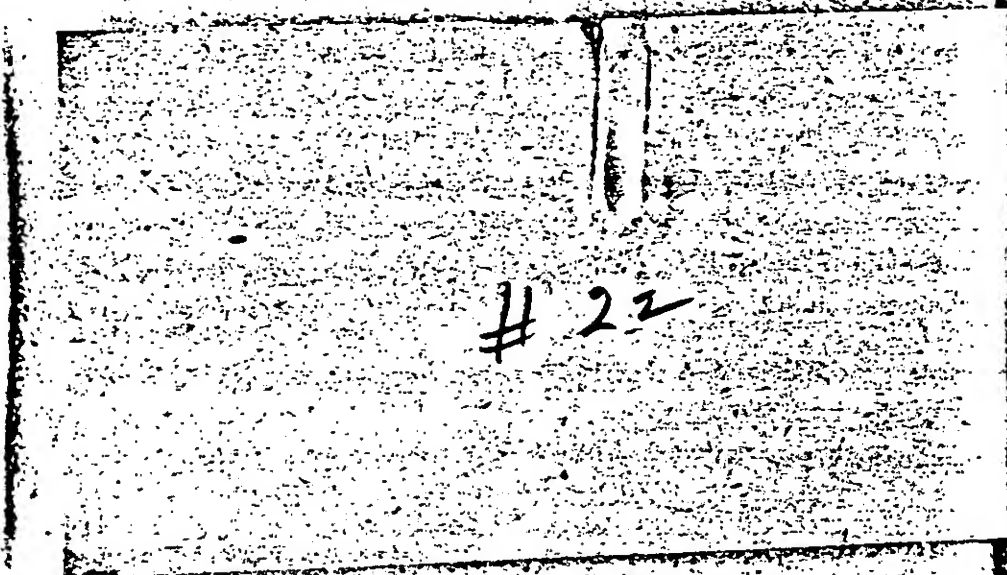
Le Xanthydrol n'est pas moins précieux pour l'analyse quantitative de l'urée. La nouvelle méthode, qui repose sur son emploi, diffère essentiellement de celles qui sont en usage par son principe et le contrôle dont elle est susceptible.

Au lieu de détruire la carbamide et de ramener son dosage à la mesure de ses produits de décomposition, nous la transformons presque quantitativement, en son dérivé di-Xanthyle, caractéristique, que nousissons

Composition du milieu employé pour le dosage de l'urée

Solution titrée d'urée	1 cm ³	20 cm ³
Acid acétique cristallisable	3,5	70
Liquide de Xanthydrol à $\frac{1}{10}$ dans	✓	10
		1.16/50

100 pour la viscosité à 29 ^{°C} & l'explication
de ce fait, qui peut paraître assez
singulier, a priori, nous est donnée par
l'analyse. Celle-ci établit que la teneur
en azote de l'urée décroît légèrement
et par conséquent aussi sa pureté, lorsque
le rapport du panthéol à l'urée
augmente dans le mélange réactionnel.



22

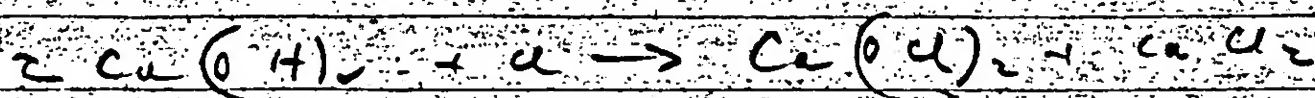
11-26-45

Time	Ca(OH) ₂ added	Time	Notes
7:30	10	15	
7:35	5	16	
7:40	4	17	
7:45	4	18	
7:50	4	19	
7:55	10	20	almost all Ca(OH) ₂ gone
8:00	5	21	
8:05	4	22	
8:10	1	23	Finish

Filter 8:20
 Drain off at 9:30
 residue
 5 min wet
 2 min dry

Titration
 $200 \times 1.5 \times 0.1047 \times 0.0358 = 1.1 \text{ gm.}$
 $\frac{1.1}{1.4} \text{ Ca(OH)}_2$

	M.W.	
Cu(OH)_2	74	4×143
Cu(OCl)_2	143	35.71
test am 0.14	88	8.7
test Am 0.14	123.5	56.5
		143.5



$$35 \times \frac{74}{143} = 2.7 \text{ am. Cu(OH)}_2$$

$$50 \times \frac{74}{143} = 4.0 \text{ am.}$$

Calculation for Cu(OCl)_2

$$10.5 \times 0.1047 \times 0.1313 = 0.0393 \text{ g.}$$

$$\frac{2.00}{0.4} \times 0.0393 = 15.7 \text{ gm.}$$

$$1 \text{ am. product} \times \frac{143}{227.4} \times 1 = 0.97 \text{ am. Cu(OCl)}_2$$

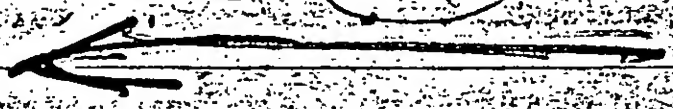
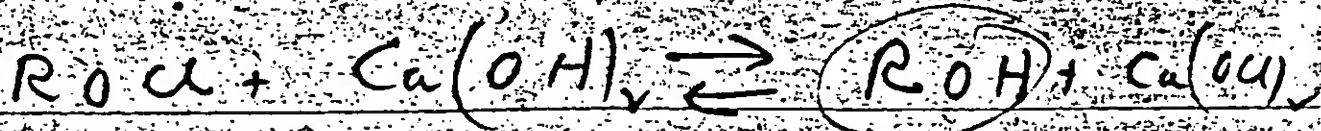
Herrules Schenkweiler 3
PE 6-6268

Du Pont 2
Orensky ST8-2020

30
60

20 060 45
100 33

33 33 9-1 later
150



1070

38.4

48.2

250

14.9

38.4

254

18.5

9.8

36

1000 116

2 Cl₂ + 2 Ca(OH)₂ → CaOCl₂ + CaCl₂ + 2 H₂O

2 x 71

2 x 74

143

111

2 x 18

142

148

2

an d - 25 gpl → Ca(OCl)₂

1618 - 0.1028 - 0.0195

0.1028

6/6/50
0.0195

215

$CC_r \times N_r \times \text{only } 5 \text{ axis } \psi$

$$44.1 \times N_r \times 0.04903 = 0.2$$

$$N_r = \frac{0.2}{44.1 \times 0.04903}$$

~~220~~

C C N x = 1000

$$8.6 \times 0.1025 = 0.8819$$

~~1.1181~~

~~2.2~~

$$0.0449$$

$$0.044$$

$$0.246$$

2890

1890

Ca(OH)₂ 3H₂O

1.9

Ca(OH)₂

$$\frac{74}{197}$$

$$\frac{7.6}{1.97}$$

C C N x = 1000

$$8.6 \times 0.1025 = 0.8819$$

Ca(OH)₂ 3H₂O

16150

0.2

22.16

5/5

Ca(OH)₂

CaCO₃

Ca(OH)₂

Ca(OH)₂

Ca(OH)₂

Ca(OH)₂

Ca(OH)₂

Ca(OH)₂

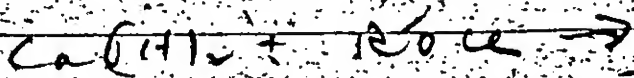
Ca(OH)₂

10/15

$$3.03 \times 0.20 = 0.606$$

$$\frac{74.10}{1.16} = 64.0$$

$$1 - 5.9 = 5.1$$



79.5

62

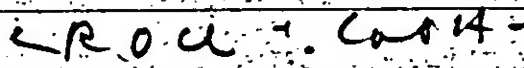
17.5

74.00 gms

$$\frac{8}{9} \times 3.5 = 3.11 \text{ gms}$$

36 gms

$$\text{actl ROH} \times 0.20 \times \frac{74.10}{17.6} = 0.84$$



$$5.6 \times \frac{54}{74} = 4.1 \text{ gms}$$

$$\frac{36}{74} = 0.486$$

75

CaCO₃ - molar 100

39 CaCO₃ - 143

to 35.5 g/l arch = 143

40 → 143

143, 250 = 27.69 CaCO₃
2x100

89

176
143

x 27.6

35.5 g

3139

1000
250

30.89
35.5

750
250

2CaCO₃ + 5H₂O → CaCO₃ + CaCO₃ + 5H₂O ↑

143
143

100 31
Ca → H₂O + 400

44 g/l
171 liter

50 250
40

143
30

24 g/l

200

143

30

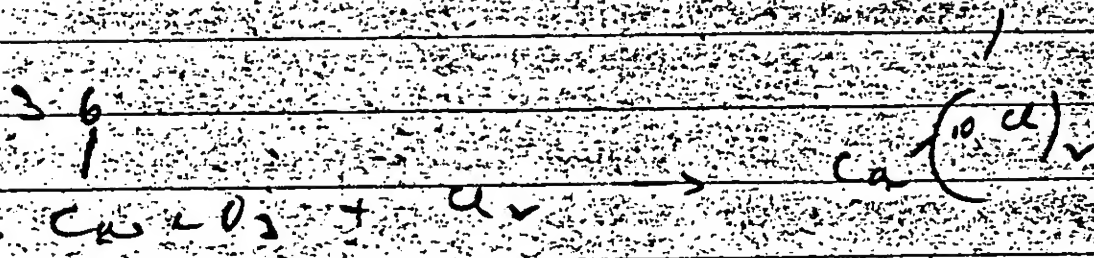
20

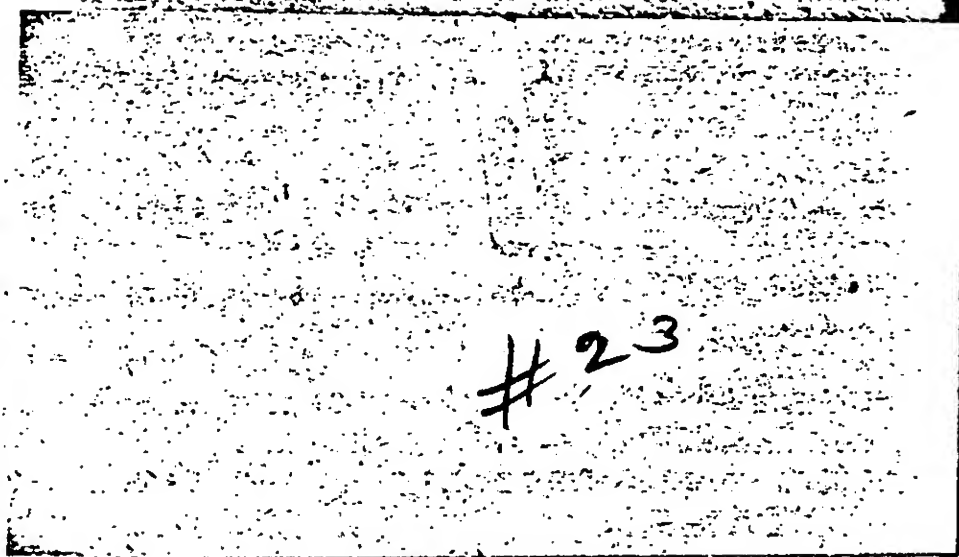
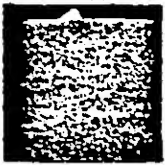
$$36 \times \frac{143}{2.10} = 2579 \text{ Ca(OH)}_2$$

$$\frac{2}{9} \times 2579 = 577.9 \text{ Ca(OH)}_2$$

$$577.9 \times 0.90 = 520.1 \text{ Ca(OH)}_2$$

$$520.1 \times \frac{74}{143} = 267.6$$





#23



Sodium Peroxide 4 oz

" Bismuthate 1 "

Ammonium Oxalate 4 "

Potassium Chromate 4 "

Potassium Thiocyanate 4 "

Potassium Chromate 4 "

D. ~~Mr. Wa^{ch} D. 5 49.00~~
~~Belmont Smelting & Refining Works~~

EXA 11-830 Labels rectangular, gummed with red border
2 boxes size 217 0.20
3 boxes " 205 0.30
11-676 Ice-Chipper 1.00

Silicone grease - 2 tubes

14-357 Scorpula Box of 6 1.00

6/6/50
200

Chemicals to order (Minimum quantities)

~~Potassium mercuri-thiocyanate~~

~~Cobalt nitrate~~

~~Magnesium Chloride~~

~~Arvin tri-carboxylic acid reagent (for detem)~~

~~9-528 Rheostat Size H (200 ohms) \$8.00~~

~~9-506A Weston ammeter 0-10 amp \$9.00~~

~~9-506C Weston voltmeter 0-5 volts 12.00~~

~~2-535 Battery, porous cups~~

~~3 Size #1 \$0.32~~

~~2 " #1.5 0.52~~

~~1 " #1.7 0.54~~

~~2-587 Beaker, nickel 350cc. 3.00~~

~~2-592 Beaker, monel metal 350cc. 4.00~~

Vill Corp 1076 Weston Model 280 Volt ammeter

50/5/2.5 volts 10/1/0.1 Amp 32.25

10-001 Finger Cots, light rubber

1 doz. med. 0.50

1 doz. large 0.50

9-191-5 1 pkg (250cc) 6 mm. Belladonna 3.25

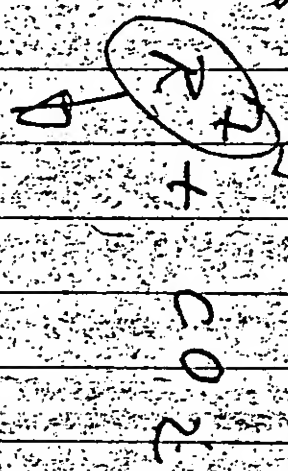
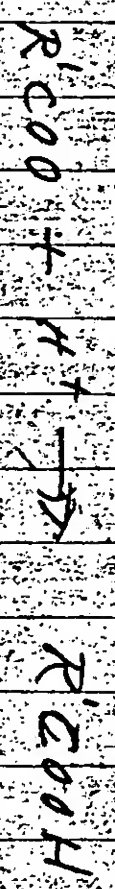
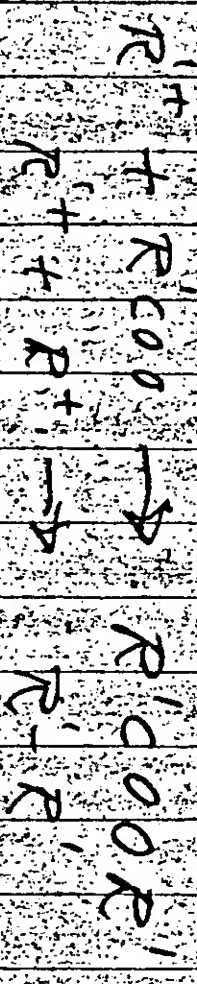
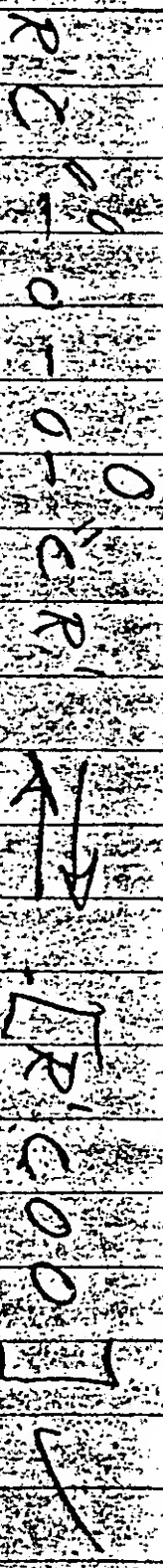
2-540 Beaker, Griffin with spout, Pyrex

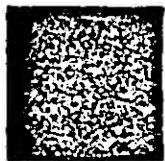
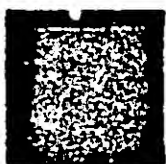
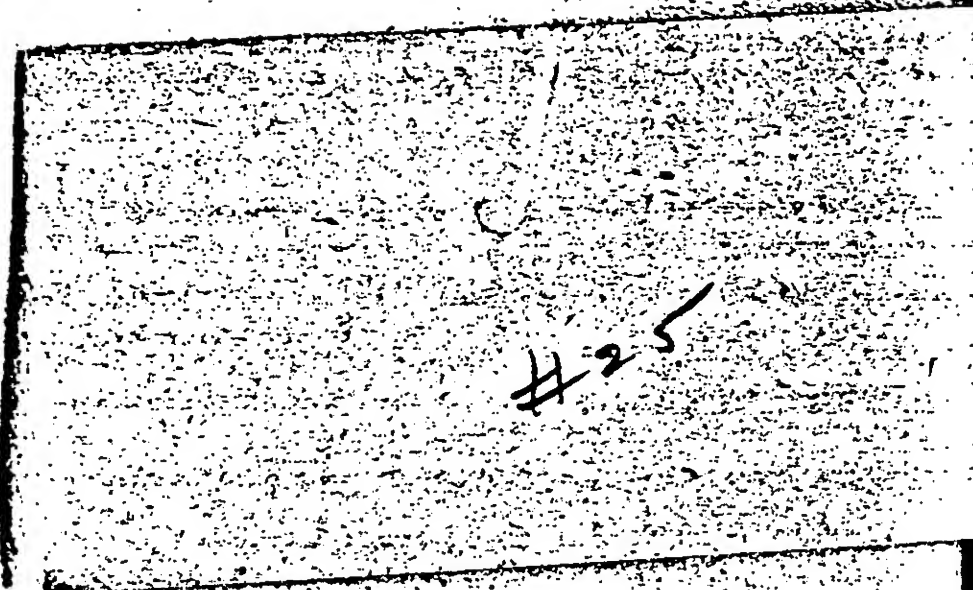
6-10 cc. 1.02 6-30cc. 1.02 6-50cc. 1.02

8-125 Crucible, Platinum without cover, size #2 (375cc) 1.00

5.00

24





Hydrograph

0.75%

26-30%

15%

Induction
period

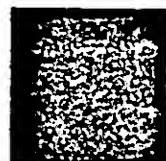
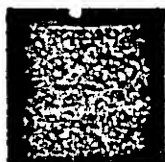
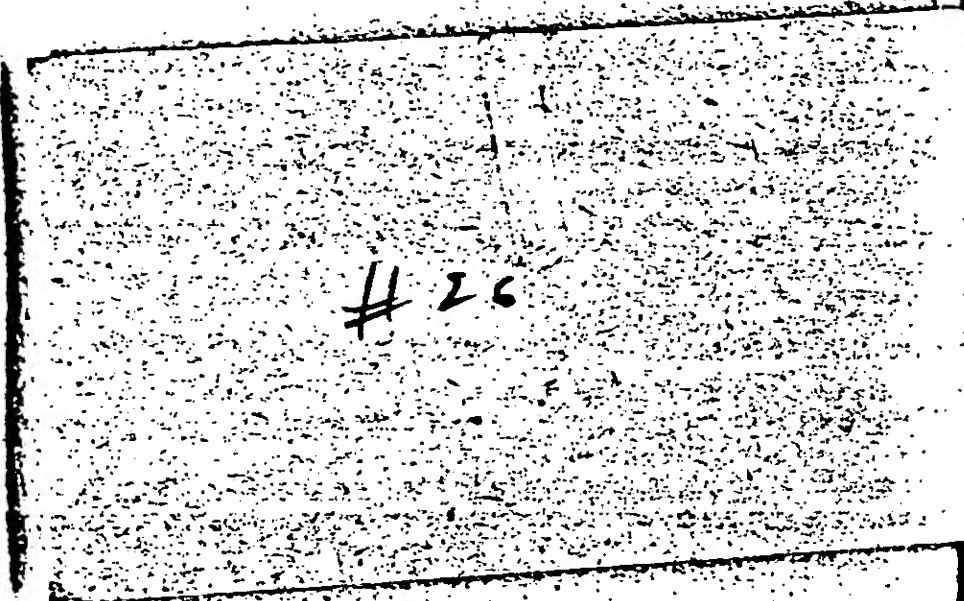
post-hypoxic

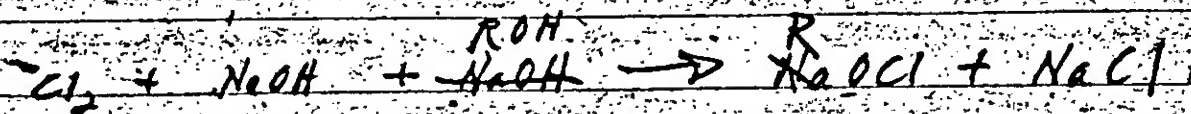
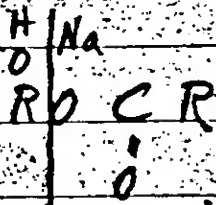
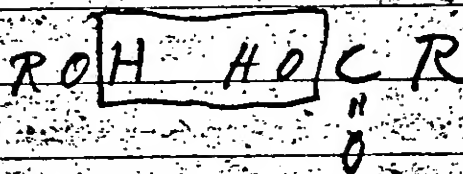
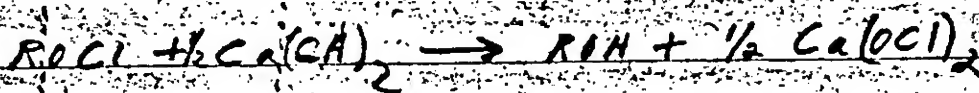
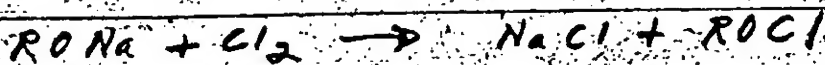
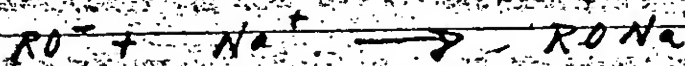
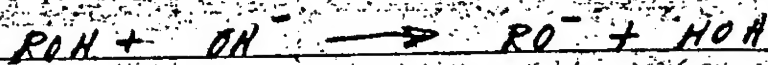
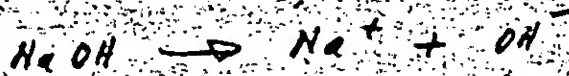
65°C
65°C
65°C

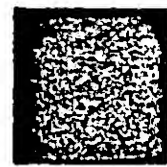
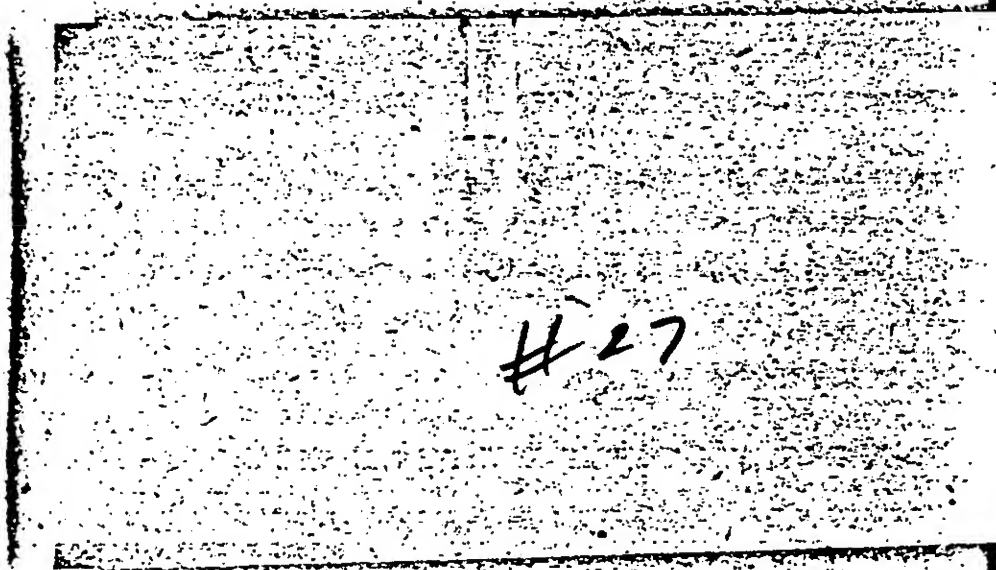
Time

65°C
65°C

Time







Specification of valves not yet ordered.
Specification of Probe levels
Instrument layout & board
Electrical layout, space arrangement
H₂S system instrumentation
Design of Furnace.
Unstalloys & reactors not based on calculation.
Stanton was not told of abandonment of
these reactors.

Promised to call Kottlieb to change terms.
Promised letter of explanation from London.
Said I will be called to sign Monday

Was never consulted on Norman deal, except
for two instances of curt and overbearing post
facts information.

Was not consulted on "cooperative".

Was not consulted on Klein-Lavy Note

Was not consulted on dissolution 1947 August

28

come with the closing
the long deal.

ear are;
Everything that we told you about the
very precarious state of the Stanton job
is exactly as we said it. It is most
essential that you return in a reasonable
time so that the job
can be properly concluded.

Further, we ^{to say} ~~believe~~ that it would
be ~~impossible~~ ^{impossible} to ~~adapt to a situation~~
~~to demonstrate (before such a situation is~~
~~developed) new methods of~~
~~the adaptation to the situation~~

develop a modification of the ~~existing~~ ^{existing} ~~process~~
process in a few days so that ~~it~~ ^{you} could
demonstrate in Liverpool.

~~It is~~ ^{However,} if ~~you~~ ^{you} deem it proper to
~~participate in the~~
extend your stay so that you will be
~~able~~ ^{able} to days in London with the
objections of

1. killing the dist woman to J.C.F.
 2. ~~kill~~ ^{kill} the ~~un-~~ ^{un-} ~~formally~~ ^{formally} ~~by~~ ^{by}
 3. ^{open} the Wolfson
- then please go ahead & do so. We

will ~~try~~ ^{try} to keep Stanton ~~in~~ ⁱⁿ
multipled here.

Harry & Phil

#29

Dear all;

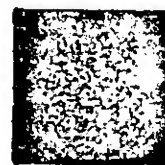
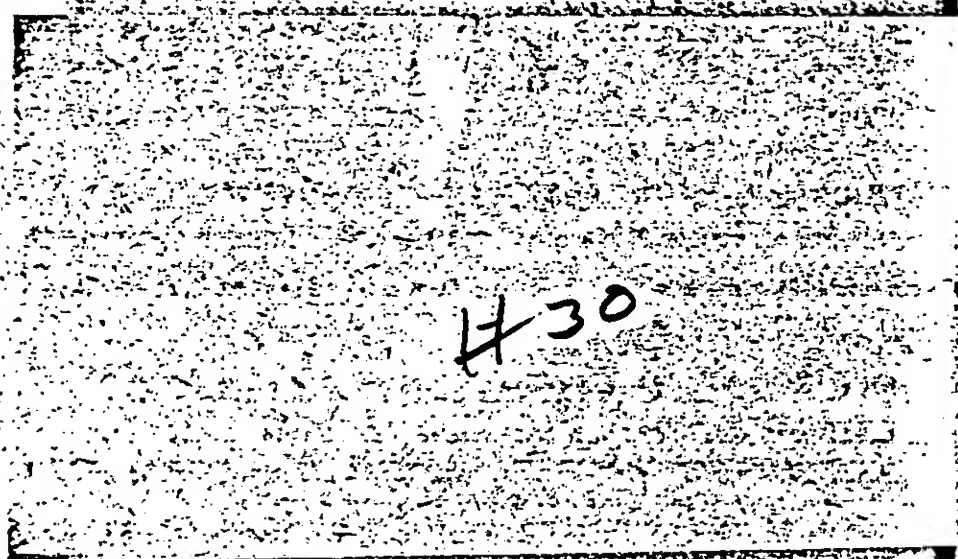
Everything that we told you about
the precarious state of the

take care

when inevitable to develop initiative of
cyn. process.

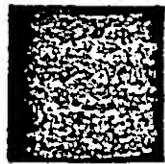
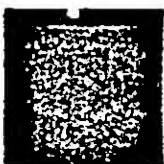
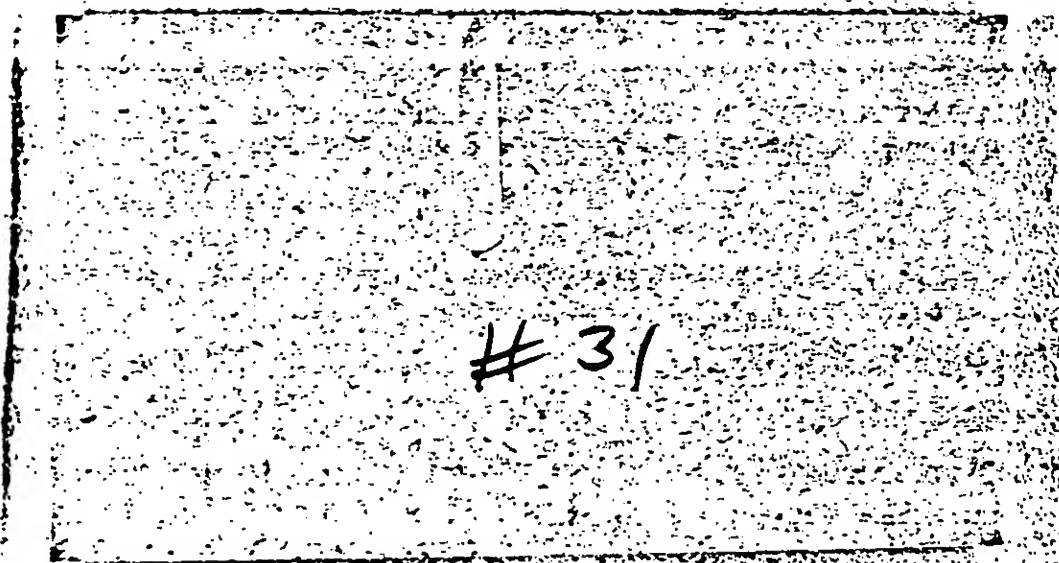
please to review for that

Ge 8-4823



Come back & finish starter deal or
we cancel! :

Next 5
Days
10.00
per hour
per hour



Th
Th
Fri
Sat



Following

6⁴⁵ AM

Let the

Health Doctor at La San

San Diego

channels

Campaign to

Campaign to Divide

16/6/50

32

Campaign of definite pattern of Stanton

A. Stanton

conscious or unconscious

1. lies on completion of job

a. End of Jan for design & drawings - not started till middle of Feb

b. Telling Stanton we had made many runs in d. reactor and that we would give him yields, quality data etc. Evidence - letters. This we did not find out till we saw Stanton's request for the data.

c. H.S. Generators - Stones are told

(1) could be purchased standard

(2) all had designed them before

(3) complete negligence to consider the problem.

d. Offering to build a plant for Burns

when the contract (Stanton) specifically forbids the sale or disclosure of such

information. Evidence - contract, and

then telling Phil & Henry that the

Stanton contract did not prevent them

from signing with anyone else in

the U.S.

e. manifold promises to Stanton on completion of various items - see above

2. Oscar - The partner was a man. If
the man was (partner) he would have been
told what was going on.

a. Norman Deal

was taking
out of the money to Oscar

b. Disruption of Partnership - we all

we must take any

c. Levy's Judgment Notes

If not then he should have been released
from the partnership arrangement and he
kept on as a paid employee.

The man worked for four years (you took
him away from his account field) & now
has nothing to show for it but a mass of
debts & 7000 in arrears. This man has
lived in your & stuck up for you & when
Phil was dubious about coming here Oscar
assured him that you were of the highest
moral fiber, Oscar alone in 1945 had
faith in your completion of the sheet
polymerization. To restore Oscar you
would have needed this man & you
know it.

Left job with at least one salary

3. Phil - Came here & worked for nine months
without pay - He'd "bro" & you borrowed that
much. Would have been on call at all
times to the extent of working any
previous that he had and now searching

salary is to be waived, as a recommendation
is to get (an increase) (-) but has decided
not for a third to strike) to 125 out the
150 are had provided & only one competition
of practically every deal in business not only
the long run & only after 6 mos. is it to be
considered. The waiving of salaries had been
brought up but Phil had not agreed to
anything & you had said that we would
discuss further with some of our
statements as to having a share in the
Co. Then we told's for with your pulled
the 150 per week gap plus the info that
we would be making more money than you
& you would be borrowing money from us
check Abe's statements as he had

125 now for Abe any evidence of faith
150 weekly (I was wrong) & we
 would have gone along,

Abe may still be involved
never were we ever consulted on anything
working is check about no going out to the
law where we belonged only reflected what
you thought

1. Harry - Have worked avg of 80 hrs / week
since have been with A.B.A. cuts & Cuts
before last Oct. Always on call. Always at the
 always at 9-10

... back to extent of 1000 to small ...
... Have sent every ... made to
... all ... as to Harry ...
... just for public consumption - never ...
... to ask (and fact talk for granted) that Harry
... all ... under the pressure of
... continuing state of emergency ...
... Eddie Q, Rudy, ...
... etc.

... as totally ...
... not saying anything (with
... etc.)

... ..

... we would be ...
... (idea advanced by ...
... to agree to
... at 5 PM ...
... talk

... I am anxious to get back to
... I would ...

... for my ...

... all talk of stock distribution ...
... look at ...
... most important, ...
... would not ...
... must ...

d. us for no
for this again - taking on of fantastic
projects for completion in incredibly short
times

3.1) Polyvinyl α -Polyvinyl acetate

(12) Longa - bird - me me prous

(6) H-T-N - _____

would ever have any time for myself. In

two yrs have never been able to see my

coming across me. and talk about my

~~being one social life is just because~~

~~Paul W. Watson~~

J. Mill - Logical as all get out. Q. mill, need

day no more. Bill apparently was not seen

acted about waiver of salary

6. Maria - new friend. best money without visit

Handwritten signature

Campanula trachelium (Beautifully striped mostly
mosses)

P. perue - complanatus. True leaf. Not printed as

other fruits - small. You expect tolerance for

your many small foliages of hemispherals, covering

up on the possible avails) so they not done for

✓ Phil - reminding other chemists work. Time but

again gives up. Va. Mtl. is other qualities, sell

Harry is a little weaker

3. Sorry -
too much about wanting to go down also
that I was not as good a chemist as one had
at first supposed.

4. Drive - hydrolysis. Was just hanging around for
something good, when Ann's vicious attack
on you right there - I got weary of you
then.

5. Sol, sub - rendering & vitification

6. Only one was crop. a unrolled up affair
if ever there was one.
Ann had. But she couldn't stand him
because he had made criticisms which
hurt & selling promises before we had them
& out of book.

II. Ann

1. All my dear relations

a. after promises to me as a starter job

b. we are only shareholders & can only advise
which so much should realize that the
cards are stacked against us.

c. Selling promises before we have them - Very
bad business while drives us to do work
hastily & poorly, & without proper looking
up

a. M. M.

b. H. T. H.

c. provided a. No. 10. 10. 10.

shall demonstrate in words in action of
957, in (from date) 10...

our protests against dealing with facts like
poor + milked + your dependence of them.
It is obvious no good work.

II - Suggestions for Future

1. Finish station for

operate on a much reduced scale. Have
Name in one place + out in two

3. It would suit to O.C.I. do so.

I - Involvement

1. Deliberate campaign to wreck your home
life.

2. Deliberate campaign to leave only a motherless
involvement controlled by reason for opposi-
tion to Name.

3. Check - you said yourself that the Name
money.

4. The fight with any one is absolutely in-
capable of attaining along with anyone -
our family

(I'm back)
and return (see his word) on all line to Carter
deal.

\$7,000
\$2,000
\$5,000

modules
1. ~~possible~~ to complete one module of daily drive
so that you

(I haven't heard from 1 since we

1. Condition in which left C.

left us without money to run office. ^{with} no money for living expense
about 10 minutes about 1000 tomorrow
most important - Stanley

very shocked, ~~maybe~~ because he wasn't
back already

to this limit of 1400 system 15,000

pet. head, to branch contract for which
he has all proceeds

8. I went with him a

see Wolfram &

for will take too long for him to demonstrate

what are you going to do?

judging from his letter he would stay
longer than a

#33

To be Done

1. Run Satterman for double
2. Chlorinate HOC6H4ONa
3. React with HOC6H4ONa with HNO3
4. Oxidize HOC6H4CH3
5. Try to get HOC6H4CH3 by OH in H2SO4
6. Prep HOC6H4CH3 in V.C. (also try HOC6H4CH3)
7. Get "Toap" in V.C. (also in H2SO4)
8. Prep "Quin" in V.C.
9. Get V.C. samples put away (ref. 6)
10. ~~Get HOC6H4CH3 in H2SO4~~
11. Carry out Toluidine tests
12. arrange samples HOC6H4CH3 for E.P.
- 13.

Petrolite

BO 9-9088

500 } Called for samples
1035 }
700 } Nov 10 '47

30 Broad St.
near Rdyg. & New St.

Wed morning

Amcon Corp.

29 Bidway

N. Y. C., N. Y.

BO 9-2668

Call Wed. morning
Mrs. Turner

55

5 Cell ✓
5 Camp ~~kill~~
10 Home ~~kill~~
5 AM ~~kill~~

25

15 week

Nov 16
E. 49

779-91 (1945)

R. Decker

KH new names

Nov. 47, 3159

R. H. in autumn

V 464

Nov

~~464~~

Water 130-140°C

NaOH + NaOH

V 464

Agta DRB 411, 0.2

→ amide & phenol

Meil V₂ p. 160

Size ^V 200



Vanderbilt

C. 1898 I 127

~~at~~ at ~~the~~ the ~~the~~ the

6 the Cook with K11

at the

F-111 133, 49



V 108

Several days to reach K11

with a


Ride C-11 53 579

the 11 359



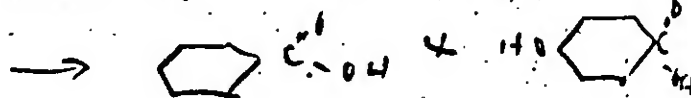
Anal. II, 325

Prep

from H_2O_2  CH_2 into a
mixture of 25% H_2O_2 and a
small amount of H_2SO_4 (D.P.P. 454, 508,
C. 1964 II, 1269).

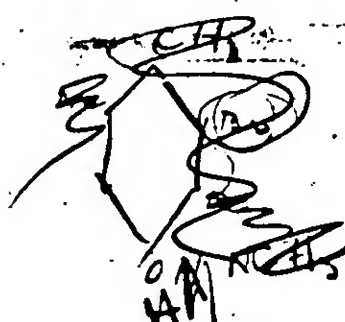
React.

Heating with KOH to
140°C @ 220-240°C

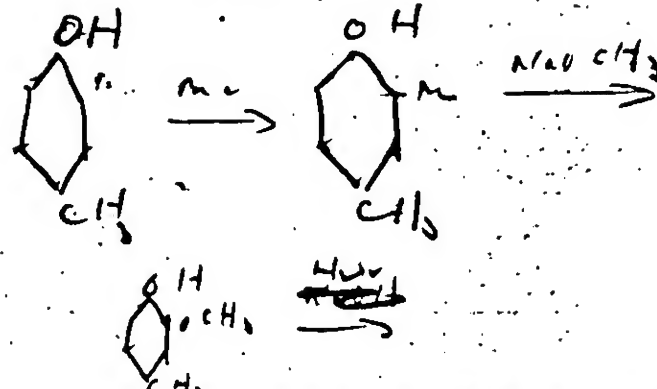
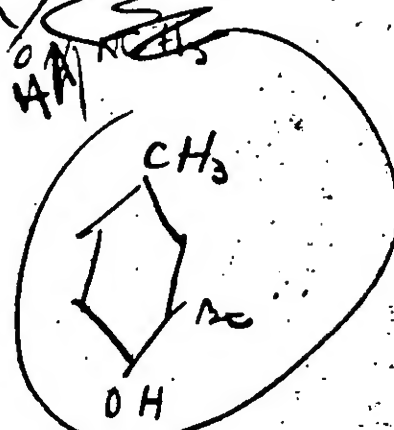


Anal. 32, 2511

Na salt - needles.



NI 464
 VI 205





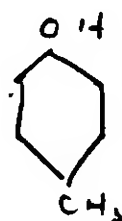
col. lig.
 b.p. 218-219°
 m.p. 57-58°
 (needles).

dist. - 16, 405
 2-methyl-p-Kresol

orig. anal.
 Liebig's ann. 320, 203
 (1902)

T. Zincke & K. Wiederhold

- Prep
1. Dissolve OH and in 5-6 times
 grams of CHCl_3 .
 2. Cool immediately.
 3. Add in this amount of NaOH .
 4. Let stand for days.
 5. Add HCl to neutralize.
 6. Wash with water from 4-5.



E

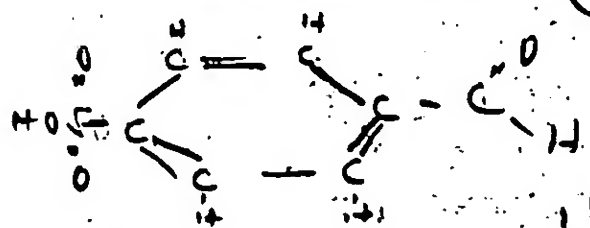
mp. 35°Z
-6 p. 12 min. = 117°

mt. 6, 411

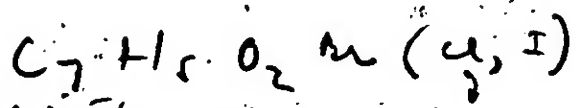
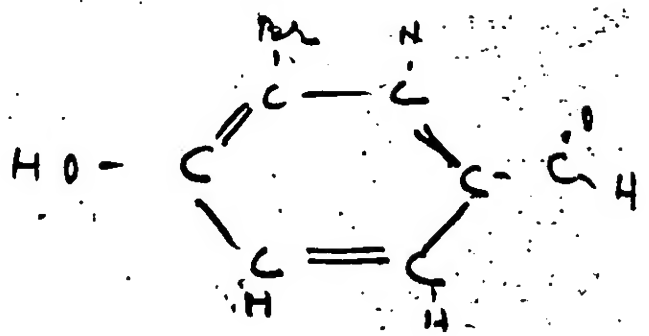
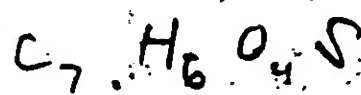
mt. 17, 2533

distill. in. distill.

p-014. acid $\xrightarrow{\text{NaOH (aq)}}$
 $\xrightarrow{\text{concentrated } \text{CH}_2}$
 p-014. I_2 $\xrightarrow{\text{keep refluxing}}$



Formel
neque



Formel neque

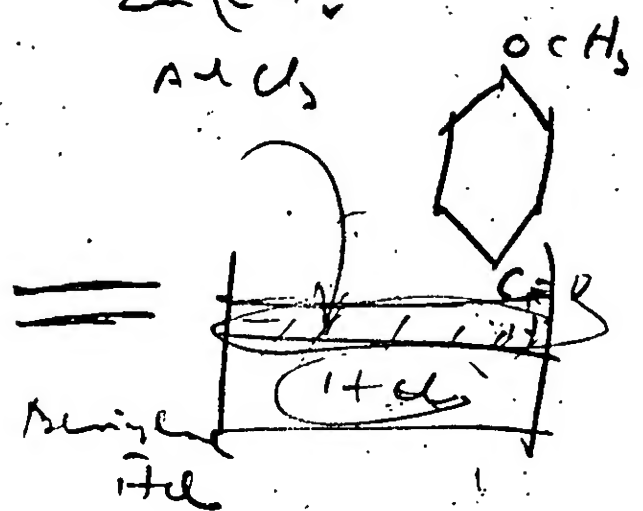
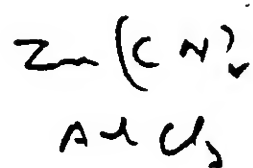
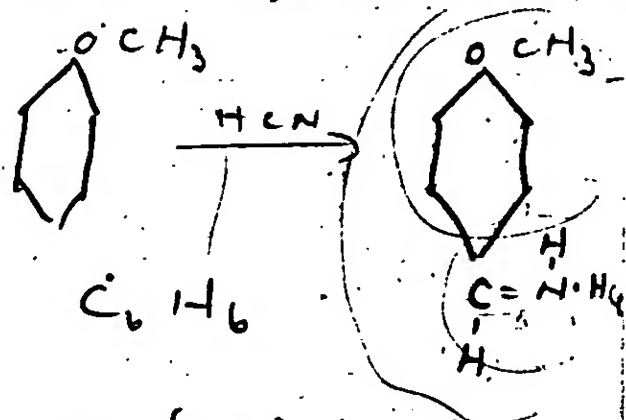
8, 54

8, 63

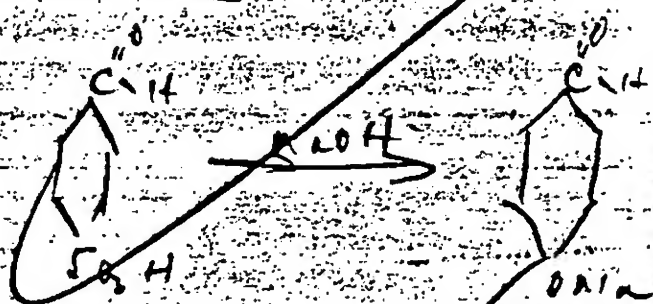
8, 82 (5, 37)

8, 81

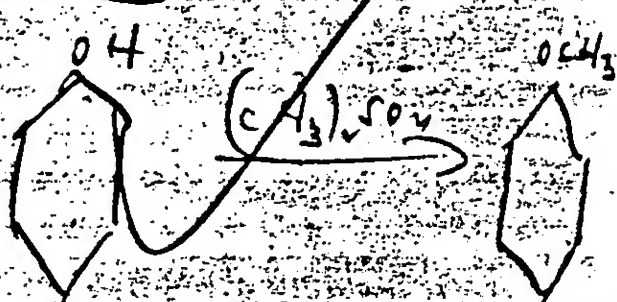
3 a, 4-014
neque



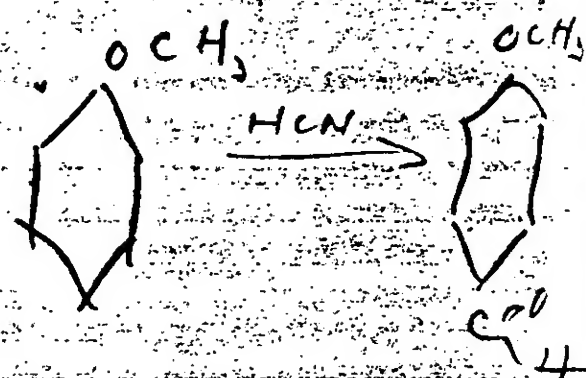
Series I



Series II

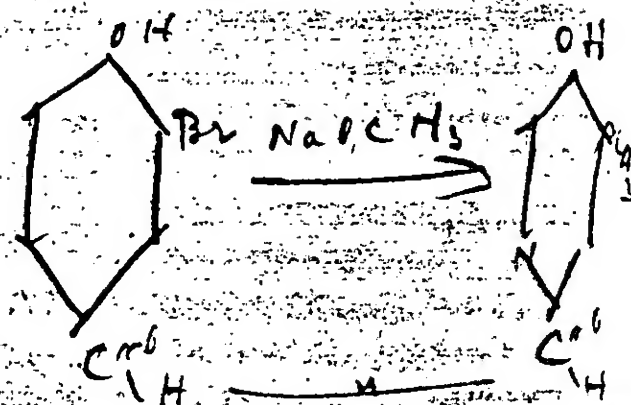


Sched III



Sched IV

atoms of mass.



C

O



9h

92



2265

$$\begin{array}{r} 2.6 \times \frac{46.1}{67} \\ \hline \end{array}$$

5h

6h.7

$$\begin{array}{r} 95 \\ \hline 67 \end{array}$$

95

$$\begin{array}{r} 11 \\ \hline 67 \end{array}$$

6/6/50
200

25
—
95

87
x



C. H. & O. H.

2
6
16
—
94

can use to inf. can get
mt. away fast.

Cont.

45-46 0.6 m.p.s.

600-900 ft

10 min. intervals

deep wells 40, 45, 50 ft

low permeability

1. May be of local type

and 2. 500 ft. deep

in deep wells

100 ft. intervals

2. Work on cat → depth
distrib. of prod.

1. P.T. not commutative
rel. probs.

2. $CO + H \rightarrow CH + O$
(also, also)

3. the P.T. distribution
170-1700 Na + CO

4. new study distribution
470-1700 / 1000000
need good test / equipment

5. pressure

Na not about atoms
not common

Ca ionization

Fe ionization

Mg ionization

(only in mild conditions)

3. can start at 4500
sawdust & lowly was
control (by varying
catalyst) -
2 Fe

Skinner used Fe and
found it was very hard
to use

- a. Co was not available
- b. Fe was not available
(catalyst) -

4. Reycle Process

Push gas thru to find
that it comes out at 100
reusable heat 100 ~~from~~ ^{per cycle}
gas to 1 per gas

(mixture)

447, *Swelling* 20 mi

117, D.O. ~~117~~ 160-70 al

77, also not 44 H
L to C

77, C₄ H₂

77, C₃

57, H₂C=C₁₁

77, *more*

5. *High Mass Peaks*

Excluded within dig. &

bubble thru gas

c. 200-2000

d. 2000

e. 2 H₂ to 1 C O

~~fracture~~ ^{but} ~~was~~ ^{which} ~~main~~ ^{carbon} ~~oxide~~

g. Set C formation —
unpredictable of bond
may be long & dense or

2. Keep p.p. of H₂ to be
near C formation

d. $2CO \xrightarrow{+H_2} C + H_2O$

Carbonide \rightarrow C-C
de-hydro
g

6. use oil cooling

7. use mostly solid catalyst
by ~~downside~~ of Co.

$$F = C(1 + Cu + Zn)$$

U.S.

1. use fluidized technique.

diffs

a. use contraction in volume

c. water desiccation

c. particle size - dia -
linear vol. dia

5. use NH_3 type catalyst

a. not thoroughly

b. Newton Tubes $\sqrt{5}$ inches dia
 $\sqrt{1}$ ft dia

Run ~~much~~ more directly
at 100 ft than any
other cuts.

10. at hi Poles

a. at over hi NW Road.

b. Run at 100 ft \rightarrow
waves of N.W. is 25,000

11. the mixed cut in
most work.

12. Cut. but 100' L

more at chain

in Idesane etc

Fe cut C₆ sand

significantly in Idesane

Synol.

Extraction Process

1. Prodn of alcs & methyl
or propyl & paraffs.
244 condns.
2. use fixed NH_3 type cat.
3. use 190-200°C
reaction

use hi very dry tail gases
use hi temp. all

4. If use 210°C & not
hi temp. all - at only
10% alcs

probably alcs are
members of olefins

alcs exclusively to
chain of alcs.

need more work on
cat durability - at
hi temp. in air & tail

6. all cats give detectable amounts
of carbonyls.

7. also all carbides.

Fe low amounts

Co small amounts

Ru none

all 7070 Co catalysts have
minimum cat.

to treat with H₂ & CO.

for Fe 100 70 Fe₂C₃

get active catalyst.

8. Fe₂C₃ catalysts -

1.6 & 1.8 for Co & Ni

& lower for Fe

8. run eff.

ver^{to} for CO in volume of
pods. but removal
pods quickly is not easy
of $\frac{1}{2}$.

run. run eff. is 1 in
operating mode

run. eff. = 1 at 300°C

9. cat durability greater for
> run

Co
at low pressures and
fouling of cat by bi-biol
scruff scales

5 other vent.

Results were for Fe.

65-1502-0-13 (3)



1-26-63 1367

1-26-63 1367

SAC, Philadelphia

7/10/50

SA T. SCOTT MILLER, JR.

HARRY GOLD, was.
ESPIONAGE - R

EXHIBIT 65-4307-1B-13 (3) (Exhibit 14)

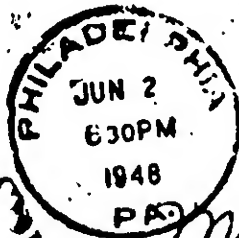
On 6/22/50, GOLD advised that this was a letter from his friend, MORRELL E. DOUGHERTY, in which DOUGHERTY must have sent GOLD about \$5.00, as this was the time that GOLD was without funds (June 1948).

TSM:HKF
65-4307

Harry -

Hope you
get this in time
See you soon.

Doc



SPECIAL DELIVERY

Mr. Harry Gold
c/o Brothman Associates
85-03 - 57th Avenue
Elmhurst, Long Island,
New York

Monell E. Dougherty
5517 Litchfield St.
Phila. 43 Pa.



6-6-50
we

65-11-30-7
4-15-1

SAC, Philadelphia

7/10/50

SA T. SCOTT MILLER, JR.

HARRY GOLD, was.
ESPIONAGE - R

EXHIBIT 65-4307-1B-13 (4) (Exhibit 15)

On 6/22/50, GOLD examined this notebook and stated that it could be in the handwriting of SHOLEM "SY" SILVERSTEIN. GOLD stated, however, that there are certain pencil notations in this notebook which are in the handwriting of GOLD himself and pertain to work while the latter was employed at A. BROTHMAN AND ASSOCIATES.

The loose papers in the notebook are in the handwriting of GOLD and BILL BOHOLL and are concerned with an experiment in trying to make methyl methacrylate molding powder.

TSM:HCP
65-4307

Pat. Jan. 28, 1941.

App. Mar. 2, 1940

2, 229, 897. — for synthesis of α -OH
isobutyric acid. — American Cyanamid Co

[I] Heating with mineral acid tends to decompose the cyanhydrin, therefore the cyanhydrin is first taken to the amide stage, then the temp. is raised for the completion of the hydrolysis.

[II]

Example =

(A) 100 parts of acetone cyanhydrin are placed in a water-cooled vessel + 132 parts of concentrated HCl are added under agitation at such a rate, that the solution temp. does not go over 30° . Continued cooling if necessary to keep temp. below 30° .

(B) After about 4 hrs, there is a 79% conversion to the amide. (After 12 hrs, practically quantitative.)

The solution of the anide is heated for 4 hrs. at 90°C , & quantitative conversion to the α -hydroxy iso butyric acid is obtained.

(C) Neutralize with NH_3 & filter off ~~crude~~ NH_4Cl .

(D) Evaporate the solution under vacuum to obtain crude ~~iso~~ acid.

(E) Purify by crystallization from benzene or distillation under high vacuum.

6/12/50
die

[Jan. 23, 1942]

α -hydroxyisobutyric acid

Purpose - - test run - hydrolyzing ~~the~~ acetone cyanhydrin to α -hydroxyisobutyric acid

Procedure (per U.S.P. 2,229,897)

[I] Quantities

For this run a pound of acid = 454 gms. is wanted - The mol. wt. of the acid is 104 gms/mol; mol. wt. cyanhydrin = 85 gms/mol

$$\frac{454}{104} = 2.29 \text{ moles/lb of acid}$$

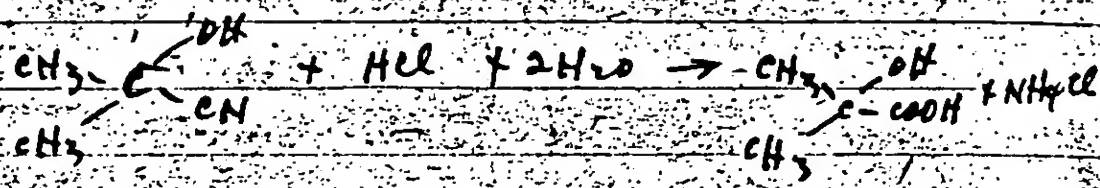
(A) cyanhydrin required - assuming a 50% yield

$$2.29 \times 85 \times 2 = 390 \text{ gms.}$$

$$\frac{390 \text{ gms.}}{0.932 \text{ gms/ml}} = 420 \text{ mls. cyanhydrin}$$

for 1 lb. α -OH isobutyric acid

(B) Requirements of HCl



Since 4.58 mols of cyanhydric are required,
4.58 mols of con. HCl are needed.

$$4.58 \text{ mols con. HCl} \times 1000 = 382 \text{ mls con HCl}$$

12 mls con HCl / liter theoretically required

However the patent calls for 132 parts con. HCl for 100 parts of cyanhydric:-

$$100 \text{ gms. cyanhydric} = 1.18 \text{ mols cyanhydric}$$

132 gms. HCl

$$1.19 \text{ gms/ml} \times 12 \text{ mols HCl} = 1.33 \text{ mols HCl}$$

1000 mls.

276/50
27

1.33

1.18

1425

5.17

12

cyan
con. HCl

6/6/50
200

1-24-47

II operations

9⁵⁰ - start adding HCl - temp. 15°

10¹⁵ - complete addition - temp. held at 25-26° during most of addition up to 31° for short period

10¹⁵ - 1⁴⁰ - ^{clear} reaction mix has a light yellow color; reaction proceeded since temp. rise occurred unless cooling was maintained

temp. range - 23° - 27°

1⁴⁰ - solution became turbid - presumably $\text{CH}_3\text{CH}_2\text{C}(\text{OH})\text{CONH}_2$ has precipitated out; no further temp. rise noted + no add. of HCl, only HCl + another organic add. probably amide

2²⁰ - start heating, at 50° the solution clears; becomes cloudy again at about 70°

2³⁵ - up to 105° lowered to 93° + maintained in range 90° - 93°

Note: a heavy white ppt. has formed

6¹⁵ - st
has
from

6³⁵ -
in
N
of NH₃ added

7²⁰

6¹⁵ - stop reaction, cool - ~~solution~~ slurry
has developed light green color, possibly
from steric

6²⁵ - down to 22° - start neutralizing
with NH_3 - cool while neutralizing -
 NH_3 required = 520 mls. - large volume
of NH_3 needed may be due to buffer action -

7²⁰ - neutralization complete

1-27-47

α -OH-isobutyric acid

Purpose - obtain α -hydroxy isobutyric acid
by hydrolyzing acetone cyanhydrin

Procedure -

(2) - Quantities

acetone cyanhydrin - 390 gms. - 420 mls. (4.58 mols)
conc. HCl - 514 g - 432 mls. (5.17 mols)

(3) Operations

12¹⁵ - start adding HCl to cyanhydrin
maintaining temp. at about 25° -
all added in about 15 minutes

3¹⁰ - first turbidity visible, & few minutes
later heavy ppt. in liquid is present -
presumably the amide

4⁴⁰ - Spiced mixture

4⁵⁰ - 90° - up to 105° for few minutes
cooled rapidly

1-28-47

α -hydroxyisobutyric acid

Purpose - Synthesis of α -hydroxyisobutyric acid from acetone cyanhydrin

Procedure -

I Quantities:

acetone cyanhydrin - 390 gms - 420 ml (4.58 mols)

con. HCl - 514 gms - 432 ml (5.17 mols)

II Operations -

1:25 - start adding HCl - temp. went over 30° to about 34° briefly - all added in $\frac{1}{2}$ hr.

4:45 - amide begins to precipitate

5:30 90° bath introduced; reactants clear when at 55°C . Ppt. again at 79°C .

1-29-47

α -hydroxyisobutyric acid

Purpose - Synthesis of α -OH isobutyric acid
from acetone cyanhydrin - using double
previous quantities

Procedure -

I Quantities -

acetone cyanhydrin - 780 gms. } 9.16
840 mls. } mols.

con. HCl - 514 gms. } 10.35
864 mls. } mols.

II Operations

10:50 - start adding HCl

11:30 - all added

2:00 - reaction mix furthest due to
ppt. amide

3:40 - start heating to 90°

3:55 - to 96° - cool

ABROTHMAN & ASSOCIATES

4/16/54
[Signature]

1-30-47

α -hydroxy isobutyric acid

Purpose - Synthesis of α -OH isobutyric acid from acetone cyanhydrin

Procedure -

[I] Quantities -

cyanhydrin - 780 gms. - 840 mls. } 9.16 mols
con. HCl - 514 gms. - 864 mls. } 4.35 mols

[II] Operations

11³⁵ - start adding acid

12¹⁰ - acid all in

2¹⁵ - ppt. appears.

4¹⁵ - cool to about 10° - 12°

+ let stand overnight with agitation.

1/31/47

[Note - ppt. did not dissolve on heating to 90°]

10²⁵ - start heating

10⁴⁵ - reached 90°

2⁵⁵ - remove bottle

Since there is an excess of 1.19 mols of HCl, 1.19 mols NH_3 will be needed to neutralize -

$$\frac{1.19 \text{ mols}}{14 \text{ mols/liter}} \times 1000 = 85 \text{ mls. conc.}$$

3³⁵ - 85 mls. NH_3 added with cooling

3⁴⁵ - filter - filtrate has deeper orange color than previous run

6/6/5

6/6/57
207

2-4-47 - Dehydration of Ester

Purpose -

attempt to dehydrate methyl α -octyl acetate assumed obtained previously with finely powdered silica gel.

Procedure -

I Quantities

60 gms. of ester

25 gms. of silica gel

II Operations

(A) refluxed for about 7 hours -

The temp. of the vapor was close to 65°C after 2 hrs. of reflux, and the mix temp. was about 77°C .

The reflux did not take place gently but in spurts. There was no strong odor of HCl at exit end of condenser.

but the flask had a very strong odor of H₂O₂.

(B) 2-~~5~~-47

Refused material was distilled:

flask temp.	bottom column	upper column	pressure
30°	32°	29.5°	94 mm
36	37	35.5	
34.5	34	29	

The distillation took only a short time, i.e. about 20 minutes. The indicated drop in temp. i.e. the last reading took place when most of the distillate had coming over, and the vapors were not sufficient to hold the thermometer to temp.

No appreciable column reflux, the there was a residue of droplets on the column walls.

2/
Distillate — 26 gms.

Residue on walls of column — about 12 g

Taken over to the pump or retained
by silica gel — about 22 g

The distillate had an odor suggestive of
methanol, the residue in the flask and on
column walls had a strong HCl odor.

6/6/54
22

2-7-47 Esterification of α -OH-isobutyric acid

Purpose - Esterification of α -OH-isobutyric acid using reflux temperature, + passing in dry hydrogen chloride.

Procedure

I Quantities

4 to 1
mol ratio { 78 gms. α -OH-isobutyric acid - 0.75 mol
MeOH to acid { 96 gms. methanol - 3.0 mole
100 gms. silica gel (finely powdered)

II Operations - (A) Dry HCl bubbled in for 8 hrs. under reflux conditions

2-10-47 (B) Distil (20 mls. MeOH added to wash fluid from filter flask to 3-neck flask). Some silica gel still in

mix

4⁵⁰ - start

<u>flask temp.</u>	<u>lower column</u>	<u>upper column</u>	<u>pressure</u>
43° - boiling begins			100 mm.

46° -	38.5°	25°	
	[cut]	30° -	100 mm.

47	42.5	32	100 mm.
----	------	----	---------

47	44	38	} holds at the point for 15 min
48	44	38.5	
52	48	44	

57	54	51	100 mm.
----	----	----	---------

60	56.5	51.5	
----	------	------	--

68	61	55.5	
----	----	------	--

70.5	62	55.5	
------	----	------	--

75	65	55.5	
----	----	------	--

78	68	57	100 mm.
----	----	----	---------

85	71	57	6/6/5
----	----	----	-------

90	74	57	me
----	----	----	----

Flank Temp.

Lower Col

Upper Col

Pres.

0.0

0.0

0.0

1.00

78

57

100

1.10

81

57

1.12

92

57

~~1.15~~

2.89 pink + Tail

2.00 tail

89 am

Run due

2.10 flash + Tail

1/2.0 tail

29.0 am

2-11-47

Esterification of α -OH isobutyric acid

Purpose - try esterification of the acid with methanol by saturating a portion of the MeOH with dry hydrogen chloride + using anhydrous H_2SO_4 to take up the water.

Procedure -

I Quantities -

4/1 mol ratio decided to use { 52 gms. α -OH isobutyric acid - 0.5 mol
64 gms. methanol - 2 mols
[dried over CaSO_4]

15.1 gms. H_2SO_4

[M.W. of $\text{H}_2\text{SO}_4 = 98$. Considering $\text{H}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$ formed and 0.5 mol of H_2O to be removed then 0.071 mols of anhydrous H_2SO_4 .

will take up 0.5 mol of water = 10.08 gms
 + 50% excess = 5.04

15.12

II operations

A 16 gms. of methanol were saturated with hydrogen chloride and added to balance of 48 gms. of methanol containing 52 gms. of α -OH-isobutyric acid and 15.1 gms. H_2SO_4 - Stirred for about 5 hours. Then heat to 50° for 2 hours.

2-12-47 [B] Distillation at reduced pressure thru Vigreux column.

Time	Flask temp	Lower column	Upper column	Pressure
2:25	26.0	25.5		24.00
2:28	26	30	27	
	33.5	30	28	24.41
about 2:50 cut	33	30	27.5	

6/6/50

Time	flask temp.	inner column	outer column	pressure	notes
3:05	38°	32°	37°	100 mm.	
3:15	41°	35°	28°	"	
3:20	43.5	36	30	"	
3:25	43	34.5	28	"	
3:30	48	41	33.5	"	
3:35	52	45	35.5	"	
3:45	60.5	53	44.5	"	
4:00	67	57	42.5	} CUT	
4:15	72	58	35		
5:45				start heating	
5:55	71.5	60	50	69 -	
6:08	72.5	60	45	50	
6:09	85	70	45	50	
6:10	83	75	60	30	
6:15	89.5	76	59.5	30	
6:20	98	85	54.5	30	
				<u>CUT</u>	

2-13-47

Esterification of α -OH isobutyric acid

Purpose - repeat esterification using using
- 1st fraction from distillation of previous run
+ portion of 2nd fraction to make up
64 gms. corresponding to 64 gms. of
methanol used in previous run

Procedure -

I Quantities -

"methanol" - 64 gms (as indicated above)
 α -OH isobutyric acid - 52 "
 Na_2SO_4 - 15.1 "

II Operations

(A) 16 gms. of "methanol" were saturated
with HCl (heat of solution evident)

(B) Reaction at room temp. of full
all constituents with stirring

start - 11 ²⁰/₄₀

end - 4 ⁴⁰/₄₀

- i.e. start heating

© Heat for 2 hours with string at 5

6/6/5
2

Distillation

Time	Flash Temp, °C	Lower Column, %	Upper Col., %	Pressure, mm	Notes
1:35 PM	27	25	25	100	
1:40	31	27	25	100	
1:45	32	28	26	100	
1:50	34	30	28	100	
1:52	36	34	30	100	Out
<hr/>					
2:12.5	41	34	30	100	
2:15	45	40	35	100	
2:17.5	65	58	45	100	out
<hr/>					
2:15.0	48	36	33	30	
2:18	55	45	40	30	
2:20	60	51	45	30	
2:22.5	62	52	45	30	
2:25	66	55	45	30	
2:28	70	58	45	30	
2:30	75	56	45	30	

2-14-47

Distillation of Product of Vapor Phase

Estimation - } weight of distilland = 231.7 gms

Time	Fask Temp	Bottom Column	Upper Column	Notes
1:47				start
1:55	29.5°	28°	26°	rapid condensate stream
2:00	32	30.5	28.5	100 mm.
2:10	35	32.5	30	" = } CUT

wt. of fraction ① = 80.1 gms.

resume distillation

2:25				100 mm.
2:40	40	35	32	" "
2:50	44	39.5	35.5	" "
3:05	48.5	46	41	" "
3:15	57	54	50	" "
3:25	wt. of remain stop to change flask & bath (odor of HCl in air) = 33.1 gms resume - 60-75 mls. left			
3:27				
3:55	64.5	59.5	52.5	slow, hardly anything coming over 100 mm.
3:57	66	61.5	55	rising

Time	Flask temp.	Lower Column	Upper column	Notes
3 ⁵⁸	65°	61°	60°	solid appears

① stop distillation to filter off H_2SO_4 -

② filtrate deposits out crystals - decant (some crystals suspended) -

③ weight of remainder = 10.6 gms.

some of which may be hydrogen about 2 grains of which were added to original distillate.

5 ³⁵		same heating		30 m
5 ³⁷	40°	39°	35°	} instead
5 ⁴⁰	37°	33°	31°	
5 ⁴¹	36	32.5	29	} 20 m
5 ⁴³	41	33	27.5	
5 ⁴⁴	50	34.5	26	- STOP

nothing coming out

contains 1 lb fraction ③ = 8.1 gms.

residue in flask = 2.2 gms.

6/6/3

Summary of Fractions

original distilland - 231.1 gms.

1 st fraction	-	80.1 gms.
2 nd "	-	118.3 "
3 rd "	-	8.1 "
residue in flask	-	2.2 "
		<u>208.7 "</u>

unaccounted for - 22.4 gms. :-
represented by precipitated salts, liquid
lost in filtration and hold-up in
column & condenser, etc.

Note : about 2 gms. hydroquinone
added to initial distilland

(1) (boils at 286.2°)

(2) very small amount of oil in
fraction (2) (about 1 gm.) and

about 2 gms in fraction ③

6/15
80

2-24-47

Estification of α -OH isobutyric acid

Purpose - reflect run of 2-4-47 using
large quantities

Procedure

I Quantities

1:4 mol ratio { 161.4 gms α -OH-isobutyric acid - 0.975 mol
125 " methanol - 3.91 "

50- [dried over CaSO_4]

29.7 gms. anhydrous Na_2SO_4

II Procedure

3125 gms. melt of 125 gms.

(A) total saturated with hydrogen
chloride. The remainder of 93.75

gms. was used to dissolve the
 α -OH isobutyric acid & to flush

the Na_2SO_4 ; then the 31.25 gm
portion of melt was added, and

the whole stirred for about 5 hours
following this heated for 2 hrs
at 50°

Start turning of room temp. - 4²⁰ PM

Stop

9²⁰ PM

then heated at 50° for 2 hrs.

Temp. - 100⁰ at 11:00 AM } 100⁰
11:00 AM } 100⁰

(B) Distillation 200 (2:15-47)

Atmospheric to strip Methanol
(then Vigreux & silicon)

Fraction 201 for 10 min. 2:50 PM Flat to

① 63° to 70° 9:30 AM 9:30 AM 9:30 AM - about

② 70° to 90° 9:30 AM 9:30 AM 9:30 AM - about

considerable refluxing at this point
molecular & some further distillate came over
indicating a high boiling residue.

Some 100-150 cc pipetted out as one

6/6/61

Na₂SO₄ filtered off -

2-26-47

Distillation under Vacuum

11¹⁰ - start heating at 100 mm.

	flask temp.	column temp.	notes
11 ²⁵	78	47	rising - 100 mm.

considerable reflux -

11 ³⁵	77	35	at steady state - 70 mm.
------------------	----	----	--------------------------

11 ⁴⁰	80	45	100 mm.
------------------	----	----	---------

11 ⁴⁵	82	39	100 mm.
------------------	----	----	---------

Note: temp. dropped - distillate still coming over

11 ⁵⁰	82	31	100 mm.
------------------	----	----	---------

11 ⁵⁵	84	44	100 mm.
------------------	----	----	---------

12 ⁰⁰	86.5	41	100 mm.
------------------	------	----	---------

reflux continuing

12 ⁰⁵	87	35	100 mm.
------------------	----	----	---------

12 ¹⁰	89	33	no circulation 100
------------------	----	----	--------------------

12 ¹⁵	75	60	
------------------	----	----	--

Time	Flask Temp	Col. Temp	Pressure
12:00	82	53	50
12:15	89	48	28
12:22	90	crystals appeared, stopped distillation 28	

1772

2-28-47

α -OH isobutyric acid

Purpose :- ~~refers to~~ hydrolysis of
cyanhydric which had been stored
in reflux

Procedure:-

I Quantities:-

~~α -OH~~

cyanhydric - 698 gms. (750 mls.)
(8.23 mols.)

con. HCl - 924 gms. (776 mls.)
(9.4 mols.)

(NH₃ to neutralize excess HCl = 82 mls.)

II Fractions

4³⁵ - started adding HCl

5¹⁰ - solid appears

5⁴² - all HCl in

3-5-47

Purification of Crude Methylal

I Assume 25% of material is the formate -
Take 2000 mls. for this run.
 $\boxed{\text{Sp. g.} = 0.871}$ $\boxed{\text{MW of the formate} = 60}$

$$\frac{2000 \times 0.871 \times 0.25}{60} = 7.27 \text{ mols}$$

the formate to be hydrolyzed

II $7.27 \times 40 \approx 291 \text{ gms. of NaOH needed}$

$$\frac{291}{30} = 970 \text{ mls. of 30% solution}$$

III Reflux for 4 hours, then take off fraction then Vigreux - $41^\circ - 43^\circ$

3-18-47.

Purification of Crude Methylal

$$\boxed{\text{I}} \quad \frac{1700 \times 0.871 \times 0.25}{60} = 6.17 \text{ mo}$$

$$6.17 \times 40 = 246.8 \text{ gms. NaOH}$$

$$\boxed{\frac{247}{30} = 8.2 \text{ or } 820 \text{ ml. of } 30\% \text{ solution}}$$

II - allow for 4 hrs.

6/6/47

3-11-47

L-α isoputyric acid

Purpose - synthesis from cyanhydrin

Procedure -

I Quantities

cyanhydrin - 430 mls.

con. HCl - 445 "

con. NH_3 to neutralize excess HCl - 43 mls.

II Operations

(A) 3-11-47

10 30

11 05

2 15

} start adding HCl

all in

flask - permit to stay at room temp.

(B) 3-12-47

11 20 - start heating to 90°

11 45 - 90° + - keep at 90° for 4 hrs.

3-20-47

Dehydration of KOH

Purpose - remove water in KOH and CaCl_2 , using xylene as a ~~ref~~ dispersion medium

Procedure

I Quantities

198 gms. KOH

66 " CaCl_2

1330 ~~1440~~ mls. xylene of which
435 mls. was enriched &
dried with CaSO_4

II Operations

10⁵⁵ AM - start heating

11¹⁷ - 110°

11⁴⁰ - 139° (at 133°, heavy bubbling
appeared, light bubbling at about 126°)

Results - satisfactory

6/6/57

3-25-47

Hexine Synthesis

Purpose - to prepare 2,5-hexyne-dial
(yields 3, 4), from acetone & C_2H_2

Procedure

I Quantities -

115 gms. KOH

66 " $CaCl_2$

450 cc. methylal

57 gms. of acetone

II Operations

The dehydrated KOH- $CaCl_2$ slurry
in xylene was washed 3 times
with ether to get rid of the xylene
The slurry - KOH- $CaCl_2$ slurry was
then transferred to the reaction
flask, most of the ether decanted

and the methylal added rapidly
only about $\frac{1}{2}$ in. deepening the
temp. between 13° & 15° .

[B] The temp. was then lowered
to 5° & acetylene passed in
for 20 minutes. The temp. was
then permitted to rise to 13° &
& the bellone passed in rapidly
and the acetylene addition resumed.

Note: During the period of temp.
rise acetylene continued to pass
out of the solution despite the
stopping of the addition.

[C] 3° - start - when all acetone
 3° - 13°
 3° - down to 10° & heat
rise started rapidly, rose
to 14° then cooled to
with bath

6/6/6

4²⁵ - slurry becoming thick
+ HEAT RISE - bath - - 28° - (up to 170°)
internal temp - 15° & rising

4²⁵ - 4²⁵ - Note - Shutting down
of the C.H. stream at this point
& heavy flushing has 2 results:
(1) the temp drops suddenly &
quickly without continuation of
the C.H. addition after the
temp drops causes it to RISE
(2) the mix becomes less fluid,
i.e. with a rapid stream of
C.H. the agitator started with
ease & when the stream was
cut off, the agitator started
to move with difficulty &
stop entirely

4²⁵ - unstable element

4³⁸ - internal temp = 7°

9-24-46

- 2) 50 g Mon
1 g BP
2 g Gum Arabic
400 g distilled water

38
190

205 to 1250 under mild reflux

As soon as peak period was reached heating was stopped and the powder was filtered. Tasted three times in beaker and then washed three times by stirring for 1 hr each time.

Molding made of this material shows very little color (yellow) but is hazy and full of bubbles.

- 3) Same as above, but heated and stirred about 20 min after peak period.

Molding more hazy than in (2), but may contain less bubbles.

1.1.120

9.25 KL

50g Mon.

2g Gum

1g BP

400 g water Saturated Salt soln (Salt in excess of Natural)

Join 500 cc. water and over 200 g of NaCl. Heat to 96°C and filtered. Temp. of filtrate about 90°C, therefore, Salt is ⁱⁿ excess of saturation at 82°C.

9.30

Temp. 85°C at mild reflux

Washed 3 times in beaker and 3 times in flask with stirring.

100g Mon

2g BP

25 g Gum Arabic

500 g water

12.15 to 1:00

Dried at 78°C overnight, then raised to 100°C for

Much of the material was lost due to agglutination which was stuck to flask. For much more the amount of water.

9-24-46

50 g Mow
1 g BP
2 g Gum Arabic
400 g distilled water

5.1
11.5

205 to 1250 under mild reflux

as soon as peak period was reached
heating was stopped and the powder
as filtered. Washed three times in
beaker and then washed three times
by stirring for 1 hr each time.

Molding made of this material shows
very little color (yellow) but is hazy and full
of bubbles.

Same as above, but heated and stirred about 70 min
after peak period.

Molding more hazy than in (2), but may
contain less bubbles.

7-26-76

D) 50 g man
2g Agar
1g BP
400 g water

1250 to 1:40

Reflux stopped at 120 while bath was 89°C

Filtrate very milky.

Much of the material stuck to the sides of flask but was easily powdered

Very little of the material are round pearls, most of it appears like being shredded.

7

~~I washed~~

Sat. salt excess salt

Det down on H₂O

100 mon

2 BP

2 1/2 gum arabic

100 g water

3

~~1% agar on water~~

10 mon

1 BP

2 gum arabic

400 H₂O

disconnect at max

100 H₂O bail

~~Agar 1%~~

10 mon

1 BP

400 H₂O

2 g Agar



100 g Mon)

2 g BP

3 g Gum Arabic

800 g Water

Started 3:45

12 45 1

Time 12 45 6

95.5

6/6/50
809

9-13-46

50 g. mon.

1.0 BP

1.5 gum Arabic

400 g water

Ran at 77-80°C

Result: ^{very} Fine powder

Burned yellow on drying (matt. fused)

9-13-46

100 g mon

2 g BP

0.8 g Gum Arabic

400 g water (distilled)

Started 11:15 Brath Mix

20	78	68	reflux start
30	85	79	

Agglomeration

100 g mon

2 g BP

1.5 g Gum Arabic

500 g water

1:35 started 7:35 at

9

50 100 gms. Monomer M12 M3

4.5 8 gms. B.P.

1.5 8 gms. Sun. active

400 200 gms. H₂O

Start 10¹⁰ PM

Temp 75° → 80°

10:30

Finish 10¹⁰ PM

9-17-46

6

100 gms. Monomer Me Me

1 gm. B.P.

3 gms. Sun arabic

800 gms. H₂O

mold

Start 12⁰⁰ NOON

Temp. 76° → 80°

Finish 1¹⁵ PM

7

100 gms. Monomer Me Me

0.5 gm. B.P.

3 gms. Sun arabic

700 gms. H₂O

mold

Start 3⁵¹

Temp. 74° → 80°

Finish 5⁵²

8

100 gm. Monomer Me Me

3.0 gm. B.P.

30 gms. Sun arabic

800 gms. H₂O

mold

Start 8²⁵ AM 8:55

Temp. 73° → 80°

Finish 8⁵²

9-16-46

100 g. man.

2d BP

4.5 g Gum Arabic

900 g water

350 to 450 at 80°

3-16-46

100 g Me Me Mo (washed)

2 g BP

4 g Gum Arabic

800 g water

11.15 started finished 12.30

Temperature 80-82°C

Coarser powder than RH; fairly uniform in size

100 g Me Me Mo (washed)

2 g BP

5 g Gum Arabic

1000 g water

Started at 145 Finished at 200

Temp. 80-82°C

Much of the polymerized mat is stable emulsion

Carman

10 }
11 } Cummings
12 }

3.1
38.4
153.6

bot (top)
154.16

9-9-46

Dissolved 153 g of NaCl in 400 g of distilled water, filtered, and added 2 g of gum arabic. Then added 50 g more with 1 g BP.

12.35 to 1.30 at 80°C

Finer powder than in cases where no NaCl was used. Washed with dist. water.

17

Same as above

2.30 to 3.30 at 80°C

Washed with NaCl soln & then with water.
(5 times)

84.79

82.59

2.20

134 (water (moisture))

19-46

13 9 14

Receiving a gain

2
2
2

4

4

4

26

4

30

2

2

2

36

4

40

50 g. Monomer

note - very early in

1 g. D.P.

40 g. Sum arabic - has puting out of hilly

400 g. - H.O.

Start 1:35 PM

Temp 71-72°C

Finish

waited

11

65-4327
EX 16

SAC, Philadelphia

7/10/50

SA T. SCOTT MILLER, JR.

HARRY GOLD, was.
ESPIONAGE - R

EXHIBIT 65-4307-1B-13 (5) (Exhibit 16)

On 6/25/50, GOLD examined the above exhibit and stated that this photostat was in connection with one of BROTHMAN's processes and that this photostat had been secured from the New York City Public Library.

EXHIBIT 65-4307-1B-13 (5) (Exhibit 17)

On the same date GOLD examined the above photostat and stated that this was another patent which had been photostated at the New York City Public Library and that this patent referred to styrene, but its use in connection with plastics rather than the Buna S. process. This patent had been photostated in connection with work being done by the BROTHMAN laboratory.

TSM:HMF
65-4307

Patented Feb. 18, 1936

2,030,901

UNITED STATES PATENT OFFICE

2,030,901

PROCESS FOR DEPOLYMERIZING ALPHA-SUBSTITUTED ACRYLIC ACID ESTERS

Daniel E. Girain, Wilmington, Del., assignor to Du Pont Viscoid Company, Wilmington, Del., a corporation of Delaware

No Drawing. Application January 10, 1935.
Serial No. 1,133

12 Claims. (Cl. 261-106)

This invention relates to a depolymerization process and, more particularly, to a method of producing a monomeric ester of alpha substituted acrylic acid from the corresponding polymeric ester.

The use of polymeric esters of alpha substituted acrylic acids for various purposes in the coating and plastic arts is known. In the use of such material there is inevitably a certain amount of scrap polymerized resin which will be wasted if it cannot be reduced to the monomeric form. This is particularly true of the resins which are used in the various turnery processes. To be able to recover monomeric ester from such scrap material is of great importance in the economical processing of these polymeric esters.

Heretofore it has been known in the art that polymeric methyl acrylate cannot be depolymerized by dry distillation, the first fraction from such distillation allegedly consisting of dimer, the second fraction trimer, and so on. Investigations have also shown that such polymeric substances as polymeric alkyl acrylates generally and even polymethacrylic acid cannot be depolymerized by dry distillation to give the corresponding monomeric compound.

An object of the present invention is to provide a simple and economical method of producing the monomeric esters of alpha substituted acrylic acid from the corresponding polymers.

A further object is to provide a method for recovering monomeric ester of alpha substituted acrylic acid from scrap pieces of the corresponding polymer such as may accumulate in the production of articles from the polymer, particularly in the production of articles by turnery processes.

The above objects are accomplished according to the present invention by heating a polymeric ester of alpha substituted acrylic acid at a temperature above its decomposition point and condensing the vapors resulting therefrom. In a practical specific embodiment the polymeric ester is heated at substantially atmospheric pressure to a temperature substantially above its decomposition point, the vapors resulting from such distillation are condensed, and the condensate is fractionally distilled to recover the monomeric ester in substantially pure form.

The following examples are given to illustrate specific embodiments of the invention. In these examples the polymeric ester is subjected to what is commonly known as dry distillation.

Example 1.—10 grams of methyl methacrylate polymer were placed in a one liter distilling flask fitted with a thermometer and a water condenser, and subjected to dry distillation over a free flame. 68 grams of liquid condensate were collected and fractionated from which 62 grams of methyl methacrylate monomer were obtained. The monomeric methyl methacrylate so collected,

polymerized to a solid resin when heated for 15 minutes at 100° C. in the presence of 1% benzoyl peroxide.

Example 2.—16 grams of n-butyl methacrylate polymer were heated as in Example 1 and 15.5 grams of distillate collected, from which 12 grams of n-butyl methacrylate monomer were obtained. This material polymerized to a solid resin when heated for 25 minutes at 100° C. in the presence of 1% benzoyl peroxide.

Example 3.—9½ grams of ethylene glycol dimethacrylate were heated as in Example 1 and 9.5 grams of liquid condensate were collected. Upon fractional distillation 8 grams of monomeric ethylene glycol dimethacrylate were obtained. This material readily polymerized when heated at 100° C. in the presence of 1% benzoyl peroxide.

Example 4.—Polymeric butoxyethoxyethyl methacrylate is dry distilled as in Example 1 and the monomer obtained by fractionally distilling. This monomer has a boiling point of 116° C. at 4 mm. pressure and is readily polymerized by heating at 65° C. for 48 hours in the presence of benzoyl peroxide.

Example 5.—Polymeric styryl methacrylate is dry distilled as in Example 1 and the condensate fractionally distilled to recover the monomer. This monomer has a melting point of 28-29° C. and is readily polymerized by heating at 65° C. for 2 days in the presence of benzoyl peroxide.

In any of the above examples the process of polymerization and depolymerization may be repeated any number of times without adversely affecting the polymerizing qualities of the monomer.

It is to be understood that the above examples are merely illustrative and that by heating any polymeric ester of alpha substituted acrylic acid at a temperature above its decomposition point the corresponding monomeric ester may be obtained. Among the esters of this class may be mentioned the following: beta-chloroethyl methacrylate, o-crotyl methacrylate, p-cyclohexyl phenyl methacrylate, decahydro beta-naphthyl methacrylate, decamethylene glycol dimethacrylate, beta-diethyl amino-ethyl methacrylate, diethylene glycol dimethacrylate, diisopropyl carbonyl methacrylate, glycol monomethacrylate, furfuryl methacrylate, isobutyl methacrylate, lauryl methacrylate, methyl allyl methacrylate, naphthyl methacrylate, o-lyl methacrylate, beta-phenylethyl methacrylate, resorcinol di-methacrylate, second n-butyl methacrylate, tetrahydrofurfuryl methacrylate, tertiary-butyl methacrylate, glycol di(alpha-butylacrylate), benzyl ethacrylate, ethyl-alpha-phenylacrylate, methyl-alpha-propylacrylate, methyl-alpha-heptylacrylate, methyl-alpha-methylphenylacrylate, ethyl-

methylcyclohexylacrylate, and propyl-cyclohexylacrylate. The above mentioned esters fully illustrate the applicability of the present invention to the class of polymerized esters of alpha substituted acrylic acid, including the alpha alkyl substituted, alpha aryl substituted, and alpha aralkyl substituted acrylic acids.

While, in the examples given above, only simple dry distillation of the polymeric ester at substantially atmospheric pressure is illustrated, the present method may be carried out at elevated pressures to effect heat-cracking prior to distillation. Also, the dry distillation may be carried out at reduced pressures, if desired. Instead of distilling as shown in the examples, so-called "flash distillation" may be employed where the polymeric ester is slowly introduced on to a highly heated surface and instantly vaporized. Variations in specific details of the dry distillation, condensation, and fractional distillation to recover the monomer in substantially pure form will occur to those skilled in the art. As will be understood, the polymeric material must be heated to a temperature above its decomposition point at the pressure employed and, generally, for economical operation, the material should be heated appreciably above such decomposition point. Specific temperatures employed must necessarily be governed by the particular polymer being depolymerized. Ordinarily the vapors of the monomeric compound will be condensed but, if desired, the vapors may be used directly with some other reactant.

The present process is useful for the recovery of monomeric ester from the corresponding polymer regardless of its source. The process is particularly useful for the recovery of scrap resin in the turnery processes where waste from scrap constitutes a major production cost item. However, the process also finds utility in the recovery of monomer either from poor quality polymer or accidentally set up material, as well as from polymer of any other source.

The fact that the monomer can be recovered by dry distillation of the polymeric esters herein disclosed is most unexpected in view of the behavior of such closely related compounds as polymeric alkyl acrylates and polymethacrylic acid. Despite the fact that the polymeric alkyl acrylates and polymethacrylic acid cannot be dry distilled to recover the corresponding monomer, yet the present process is applicable to the whole class of polymeric esters of alpha substituted acrylic acid as far as can be ascertained from the behavior of the esters herein disclosed.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that the invention is not limited to the specific embodiments thereof except as defined in the appended claims.

I claim:

1. Method of producing a monomeric ester of an acrylic acid substituted in the alpha position by a hydrocarbon radical which comprises heating the corresponding polymeric ester at a temperature above its decomposition point.

2. Method of producing a monomeric ester of an acrylic acid substituted in the alpha position by a hydrocarbon radical which comprises heating the corresponding polymeric ester at a tem-

perature above its decomposition point and condensing the vapors resulting therefrom.

3. Method of producing a monomeric ester of an acrylic acid substituted in the alpha position by a hydrocarbon radical which comprises heating the corresponding polymeric ester at a temperature above its decomposition point, condensing the vapors resulting therefrom, and fractionally distilling the condensate to recover the monomeric ester in substantially pure form.

4. Method of producing a monomeric ester of alpha alkyl substituted acrylic acid comprising heating the corresponding polymeric ester at a temperature above its decomposition point and condensing the vapors resulting therefrom.

5. Method of producing a monomeric alkyl ester of alpha alkyl substituted acrylic acid comprising heating the corresponding polymeric ester at a temperature above its decomposition point and condensing the vapors resulting therefrom.

6. Method of producing a monomeric ester of methacrylic acid comprising heating the corresponding polymeric ester at a temperature above its decomposition point and condensing the vapors resulting therefrom.

7. Method of producing monomeric methyl methacrylate comprising heating the corresponding polymeric ester at a temperature above its decomposition point and condensing the vapors resulting therefrom.

8. Method of producing monomeric methyl methacrylate comprising heating the corresponding polymeric ester at a temperature above its decomposition point, condensing the vapors resulting therefrom, and fractionally distilling the condensate to recover the monomeric ester in substantially pure form.

9. Method of producing a monomeric ester of alpha aryl substituted acrylic acid comprising heating the corresponding polymeric ester at a temperature above its decomposition point and condensing the vapors resulting therefrom.

10. Method of producing a monomeric ester of alpha aralkyl substituted acrylic acid comprising heating the corresponding polymeric ester at a temperature above its decomposition point and condensing the vapors resulting therefrom.

11. Method of producing a monomeric ester of an acrylic acid substituted in the alpha position by a hydrocarbon radical which comprises heating the corresponding polymeric ester at substantially atmospheric pressure and at a temperature above its decomposition point, condensing the vapors resulting therefrom, and fractionally distilling the condensate to recover the monomeric ester in substantially pure form.

12. Method of producing monomeric methyl methacrylate comprising heating the corresponding polymeric ester at substantially atmospheric pressure and at a temperature above its decomposition point, condensing the vapors resulting therefrom, and fractionally distilling the condensate to recover the monomeric methyl methacrylate in substantially pure form.

13. Method of producing a monomeric ester of an acrylic acid substituted in the alpha position by a hydrocarbon radical which comprises heating the corresponding polymeric ester under reduced pressure and at a temperature above its decomposition point and condensing the vapors resulting therefrom.

DANIEL E. STRAIN

65-4310-7
EX 1-7

SAC, Philadelphia

7/10/50

SA T. SCOTT MILLER, JR.

HARRY GOLD, was.
ESPIONAGE - R

EXHIBIT 65-4307-1B-13 (5) (Exhibit 16)

On 6/25/50, GOLD examined the above exhibit and stated that this photostat was in connection with one of BROTHMAN's processes and that this photostat had been secured from the New York City Public Library.

EXHIBIT 65-4307-1B-13 (5) (Exhibit 17)

On the same date GOLD examined the above photostat and stated that this was another patent which had been photostated at the New York City Public Library and that this patent referred to styrene, but its use in connection with plastics rather than the Buna S. process. This patent had been photostated in connection with work being done by the BROTHMAN laboratory.

TSM:HKF
65-4307

Patented Sept. 26, 1944

2,359,212

UNITED STATES PATENT OFFICE

PROCESS FOR DEPOLYMERIZING POLYSTYRENE

Joseph C. Frank and James L. Ames, Midland, and
Albert F. Straubel, Auburn, Mich., assignors to
The Dow Chemical Company, Midland, Mich.,
a corporation of Michigan

No Drawing. Application September 17, 1941.
Serial No. 411,150

3 Claims. (Cl. 260-569)

This invention relates to a method for the depolymerization of polystyrene to produce low molecular weight styrene polymers and monomeric styrene.

In the commercial preparation and use of solid resinous polystyrene, e. g., for the manufacture of molded articles, a problem of economic importance is the utilization of trimmings, off-grade batches, and other types of scrap material. One method that has been suggested for the profitable utilization of such material is its depolymerization to the lower polymeric forms by heating. Such depolymerization of polystyrene has also been shown to be of importance as one step in a method for the recovery of styrene from drip oil, cracked petroleum fractions, and the like, where the styrene is present in low concentrations and usually associated with other compounds boiling over the same range as styrene. Thus, a styrene-containing fraction obtained from such sources may be treated to polymerize the styrene to a high molecular weight product which may then be separated from the fraction and depolymerized by direct heating to styrene and lower polymers which may then be purified or utilized in known manner.

The pyrolysis of polystyrene has not heretofore been commercially feasible due principally to the extremely low heat conductivity of polystyrene and the consequent difficulty of heating the main body of the material without overheating the outer layers. It has been shown that when the depolymerization is carried out by heating the polystyrene under vacuum to remove the styrene and lower polymers rapidly from the hot zone, a longer heating period is required and little, if any, decrease in the amount of by-products formed is obtained. When the pyrolysis is carried out by such previously known methods there are formed, in addition to styrene and its lower polymeric forms, appreciable quantities of undesirable hydrocarbons, e. g., 1,3-diphenylpropane, 1,3,5-triphenylbenzene, 1,3,5-triphenylbenzene and toluene, together with ten to twenty per cent of tarry residue.

We have now found that polystyrene may be depolymerized rapidly and with the production of only minor amounts of by-products by subjecting it to the action of superheated steam. The depolymerization is usually carried out by placing the polystyrene in a vessel fitted with a condenser and receiver and intimately contacting the superheated steam with the solid polystyrene may be broken up and fed continuously into the depolymerization vessel and be subjected to the action of steam in the solid or semi-

solid state. Liquid polymeric styrene may be run into the depolymerization vessel and superheated steam blown through the liquid or it may be treated with steam counter-currently in a tower. The monomeric styrene vapors, together with considerable amounts of the lower polymeric forms of styrene and the steam may be condensed and collected in the receiver or they may be fractionally condensed to separate the lower polymers from the styrene.

The depolymerization is usually carried out at atmospheric pressure, although higher or lower pressures may be used. If desired, steam at a temperature between 350° and 600° C., preferably between 380° and 450° C., is used in the process. Although the amount of steam used relative to the amount of polystyrene depends upon several factors, e. g., the rate of flow of the steam, the degree of contact between the polystyrene and the steam and the particular temperature used, it is usually from five to twenty-five times the weight of the polystyrene and may be more or less than this amount.

The oily layer in the receiver may be separated from the aqueous layer and treated in any suitable manner, e. g., by steam distilling, to separate the monomeric styrene. Lower polymeric forms of styrene may be fed back into the process to produce additional monomeric styrene. If desired, or the oil remaining after steam distilling the monomeric styrene may be fractionally distilled to isolate fractions rich in a single lower polymer of styrene, e. g., the dimer, the trimer, or the tetramer, which may be collected as final products.

The following examples will serve to illustrate the principles of the invention, but are not to be construed as limiting its scope.

EXAMPLE 1

4.90 grams of polystyrene was placed in an iron reactor fitted with a condenser and receiver. 60.760 grams of steam at a temperature of 350° C. and at atmospheric pressure was passed through the reactor. 4.684 grams of oily material were separated from the water in the receiver. This was a recovery of 93.4 per cent based on the polystyrene used. The oily layer from the receiver was fractionally distilled to recover monomeric styrene. There was thus obtained 2.50 grams of the latter compound of 23.1 per cent purity or a 51.4 per cent yield on the basis of the polystyrene started with. The residue from the fractional distillation was fed back into a subsequent depolymerization experiment.

Example 2

5485 grams of polystyrene was treated with 50,370 grams of steam at 340-360° C. and at atmospheric pressure as in Example 1. The oily layer which collected in the receiver weighed 6185 grams which was a recovery of 84.5 per cent on the basis of the polystyrene used. The oily layer was fractionally distilled and found to contain 52.6 per cent of monomeric styrene, 22.3 per cent of dimeric styrene, 18.8 per cent of trimeric styrene, and 3.4 per cent of tetrameric styrene.

Other modes of applying the principle of our invention may be employed instead of those explained, change being made as regards the method herein disclosed, provided the step or steps stated by any of the following claims or the equivalent of such stated step or steps be employed.

We therefore particularly point out and distinctly claim as our invention:

1. The method which comprises heating polystyrene to a depolymerizing temperature between 250° and 600° C. by passing superheated steam of at least as high a temperature into contact therewith and condensing the styrene which is evolved together with the steam.

2. In a method of depolymerizing polystyrene, the steps of heating the latter to a depolymerizing temperature between 300° and 450° C. by passing steam which has been superheated to a temperature higher than the depolymerizing temperature into intimate contact with the polystyrene, condensing the evolved depolymerization products and fractionally distilling the latter to recover therefrom a fraction of styrene and another fraction of dimeric styrene.

JOSEPH C. FRANK
JAMES L. AMOS
ALBERT F. STRAUBEL

8/5/83
65-4307

65-4307-12-13 (2)

SAC, Philadelphia

7/10/50

SA T. SCOTT MILLER, JR.

HARRY GOLD, was.
ESPIONAGE - R

EXHIBIT 65-4307-1B-13 (7) (Exhibit 18)

On 6/25/50, GOLD identified this booklet as having been obtained from the BROTHMAN laboratory sometime while he was employed there. He said this booklet is merely one of government specifications on plastics.

TSM:BRF
65-4307

65-4307
EX 19

SAC, Philadelphia

7/10/50

SA T. SCOTT MILLER, JR.

HARRY GOLD, was.
ESPIONAGE - R

EXHIBIT 65-4307-1B-13 (8) (Exhibit 19)

On 6/22/50, GOLD examined the above material and stated that it was concerned with the patent applied for by BROTHMAN in connection with the thioglycolic acid process used in the STANTON LABORATORY.

GOLD stated that the copy was given to him for him to check.

TSM:HKP
65-4307

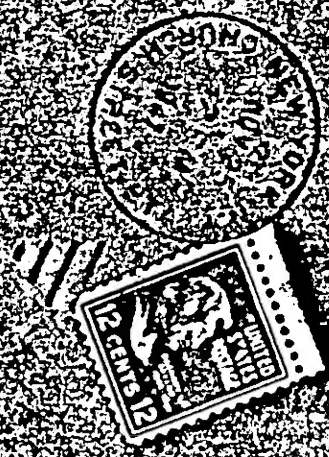
THE COOPER ALLOY FOUNDRY CO.

BLVD. ST. & MARKET AVE.

HILLDALE, P. N. Y.

PRICE REVISION

A. ANDERSON & ASSOCIATES
2010 1ST AVE.
LONG BEACH, CALIF. 11
ATTENTION: PURCHASING DEPT.



MEMORANDUM FOR THE PREPARATION OF THIOGLYCOLIC ACID
PATENT PAPERS

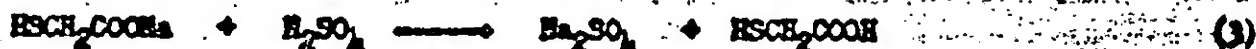
THE INVENTION

Our invention consists of a continuous process for the manufacture of thioglycolic acid by the following steps:

1. Saturating a solution of NaOH with H_2S under "super-atmospheric" pressures to form a solution of sodium hydrosulfide containing a sharp excess of H_2S in solution. (See Equation #1 below.)

2. Reacting the sodium hydrosulfide solution containing the excess of H_2S as obtained from #1 above with an aqueous solution of sodium chloracetate, maintaining the reaction system under a pressure of H_2S equal to that at which the NaOH solution was originally saturated. (See Equation #2 below.)

3. Subjecting the reaction product liquor obtained from #2 above to a "flash" relief from the excess H_2S by leading the liquor from #2 above to a flash column operated under atmospheric pressure and by simultaneously establishing contact in the column between the product liquor from #2 and an excess of H_2SO_4 . (See Equation #3 below.)



THE ADVANTAGES OBTAINED BY OUR INVENTION

The advantages offered by our invention over all previously described methods of producing thioglycolic acid are:-

1. A lower raw materials cost per pound of finished product which reflects a higher yield from chloracetic acid, soda ash, caustic soda and H_2S .
2. Absolute and assured uniformity of performance of the process.
3. Freedom from appreciable amounts of chloracetic acid, glycolic acid,

and thioglycolic acid as impurities in the final product, thereby permitting isolation of the end product in commercially useable form by an extraction operation alone, rather than by an extraction operation followed by a distillation operation. (Note:- The isolation of thioglycolic acid from the above-mentioned impurities by distillation is an exceedingly difficult and costly operation.)

4. Complete freedom from dithioglycolic acid in the end product, thereby eliminating the cost of reducing this impurity to thioglycolic acid.
5. Complete freedom from obnoxious odors through the operation of a closed system involving recycling of the excess HgS .
6. For any given plant capacity, a lower cost for plant equipment in view of the extraordinary yields obtained by us and in view of the smaller size equipment involved in operating the process on a continuous production basis.

DESCRIPTION OF THE INVENTION

The following is a description of the process as laid out on Flow Sheet #SL-B-101 for a plant with a production capacity of 30,000 lbs. per month of thioglycolic acid, based on a 25-day month and an 8-hour day.

The Preparation of Sodium Chloracetate

The preparation of the requisite sodium chloracetate is a batchwise, semi-automatic operation involving:

1. The automatic charging of the vessel, K1, with a required amount of water-of-solution.
2. The manual charging, guided by the instrumentation attached to K1, of the required amount of chloracetic acid and the dissolution of the same in the water-of-solution.
3. The automatic addition of soda ash crystals to K1 to convert the chloracetic acid to sodium chloracetate.

Upon receipt of an electrical impulse from Level Instrument, C2,¹ which impulse is obtained by the barring of the lower probe member of this instrument, water is admitted through Valve V1 to the height of the upper probe member of C2. Simultaneously with the opening of Valve V1 and for the duration of the water-filling operation, the annunciator, C45, is sounded, calling the operator's attention to the necessity of charging the unit K1 with the appropriate amount of

chloroacetic acid.

The Level Instrument, C3, the lower probe of which is located at the same level as the lower probe of C2 will, upon baring of its lower probe, set up a flow of current from power supply to A' through B' to ground, which condition of flow will persist until the charging of the proper amount of chloroacetic acid to K1 results in the submerging of C3's upper probe member, at which time the flow of current to A' through B' is interrupted and a flow from power supply to C' through D' to ground is established as the condition in force until an exhausting of K1's contents bares C3's lower probe again.

It will thus be seen that the lowering of the liquid level in K1 to the level of the lower probes of C2 and C3 initiates the charging of K1 with an appropriate amount of water, (as defined by the vertical distance between upper and lower probes of C2) and the starting of the agitator drive of K1 (via the flow of current in C3 to A' through B' to ground) through the activation of the pilot switch in the starter member of the power supply circuit for the agitator drive via the parallel power supply for the pilot switch through "A".

2/ Level Instrument C2 is a standard, commercial, electronic instrument of the "pump-up" type manufactured by the Photoswitch Co. Referring to the wiring diagram for K1 and with particular reference to the wiring diagram for the instrument, C2, it will be noticed that C2 is essentially a two-wire type control. The sensitized elements of the instrument consist of two probes, each of which is located at appropriate levels in a tank chamber. The essential nature of the electrical circuit involved is such that alternative closing of two distinct and alternative two-wire circuits is alternatively signalled by each of the two probes. The closing of the circuit between either probe and its conjunctive ground involves, through a lock-in type relay, the closing of one circuit and the opening of the other. In C2, from the time of submergence of the upper probe to the time of baring of the lower probe, current flows from power supply to A through B to ground. When the lower probe is bared again, current flows from power supply to C through D to ground, (while the previously-mentioned circuit is signalled into an open position), until the upper probe becomes submerged.

In series with the aforementioned pilot switch is the signal light, C1, which by remaining lit through the period from the initiation of water-filling to the completion of the chloracetic acid addition (until the upper probe of C3 is submerged), guides the manual addition of this material by the attendant laborer from barrels brought up by him from raw material storage by the traveling hoist. The filling of K1 with an appropriate quantity of chloracetic acid will cause the submersion of the upper probe member of C3 and the establishing of a flow of current from power supply to C' through D' to ground, while simultaneously interrupting the flow of the alternative circuit to A' through B' to ground.^{2/}

From the wiring diagram from C3 and from the fact that the circuit from power supply to C' through D' to ground remains in force for the entire period from the submersion of the upper probe member of C3 to the baring of the lower probe member of C3, it will be seen that the relay, C6, is thrown into action for the whole period starting from the completion of the addition of the requisite amount of chloracetic acid to the exhausting of the contents of K1. The actions of the relay, C6, are:

1. Through the power contacts "F", it conditions the master switch circuit (see the wiring diagram for relay C8), thus imposing upon that circuit the condition that it cannot be brought into force without addition of the chloracetic acid to K1.
2. Through the power contacts, "G", it conditions the circuit for the application of heat to the contents of K1, (see wiring diagram for V7), thereby eliminating the possibility of the waste of steam thru the heating of either a charge of water or an empty tank in K1.
3. Through the power contacts, "H", it qualifies the circuit for the starting of Pump P1, eliminating the possibility of starting up the Pump P1 without completing the chloracetic acid addition cycle. It will be seen from the wiring diagram for the pilot switch, C7, and the valve, V2, that the timer, C5, and the relay E8 in the master switch circuit, become thereby the only possible interrupting factors for the starting up of the Pump P1 and the opening of the Valve, V2. That is to say, all other conditions upon the master switch

^{2/} It will thus be seen that C3 functions essentially in reverse sequence to that described for C2, and is therefore called a "pump-down" unit.

circuit having been fulfilled, the activation of F1 and V2 must still wait upon the completion of the soda ash addition operation as guided by C5.

- a. Through the power contacts, "I", it initiates the operation of the Timer, C5.

Since the Timer C5, in its turn, does the following:

- a. Through the power contacts, "J", it closes the circuit for the vibrator component, C6, of the constant-rate-solids-feed-device attached to the soda ash hopper E2, it provides for the addition of the soda ash in prescribed quantity over a prescribed period.
- b. Through power contacts, "K", it interrupts the circuit for the pilot switch, C7, and the valve, V2, thereby preventing the starting-up of feeding of the contents of K1 to the system prior to completion of the soda ash addition cycle.
- c. Through the power contacts, "B", it closes the parallel power supply circuit of the pilot switch for the agitator, K1, thereby providing for the passing of the activation of the agitator drive of K1 from the dead circuit from A' through B' to ground, to the live circuit from C' through D' to ground, (thus providing for the maintenance of agitation thru the period of the soda ash addition cycle).
- d. Through the operation of the power contacts, "E", it provides for the conditioning of the master switch circuit (see wiring diagram for relay C8) to the end that the plant cannot be set into operation until the soda ash addition cycle has been completed.

The stoichiometric equivalent of soda ash to the amount of chloracetic acid added to K1 is added over a period of one hour at a constant rate through the constant-rate-solids-feed-device attached to the soda ash hopper, E2. Both the period of addition of the soda ash and the use of the constant rate addition principle guard against a "frothing over" through the generation of CO_2 .

A study of the above-described circuits will indicate that:

1. The replenishing of the supply of sodium chloracetate is automatically signalled, upon the exhaustion of the previous batch of sodium chloracetate solution. This occurs in stages involving the following sequence:
 - a. Automatic addition of the requisite amount of water;
 - b. The signalling of the operator to add the required amount of chloracetic acid while providing for the guiding of the operator in adding the requisite amount of chloracetic acid;
 - c. The automatic raising of the temperatures of the mass in K1 to the desired 50 C. during the progress of the soda ash addition opera-

tion, thereby providing for the readiness of the batch of sodium chloracetate for addition to the system upon completion of the soda ash addition cycle, by providing for the completion of the reaction to form the sodium chloracetate.

- a. The automatic addition of the requisite amount of soda ash subject to the qualification that the chloracetic acid has been previously added in the required amount.
2. Provides safeguards against:
 - a. The wastage of steam in heating either an empty tank or a batch of water in K1.
 - b. The starting up of the plant without the operator's having made the addition of the chloracetic acid in the required amount to K1.
 - c. The starting up of the plant without having carried out the conversion of the chloracetic acid to sodium chloracetate.
3. Confines the period of operation of the agitator to the period during which chloracetic acid is being dissolved in water and the period during which the chloracetic acid is converted to sodium chloracetate.

There remains now but to mention that the maintaining of the influent stream of sodium chloracetate at the required temperature for the optimum effecting of the sodium chloracetate-sodium hydrosulfide reaction, namely 50°C ., is accomplished through the "on-off" control of Valve V7 through the temperature control C33, which is the sole controlling factor over the operation of Valve V7 through power contacts "O" of the relay, O6, after the initiation of soda ash addition cycle up until the exhaustion of the prepared batch of sodium chloracetate has been exhausted. The operation of a plant producing 30,000 lbs. of thioglycolic acid per 8-hour day, 25-day month, and based upon the preparation of a single batch of sodium chloracetate to provide for the entire shift, involves:

1. The preparation of 62½ gals. of sodium chloracetate solution made up through the addition of 1,940 lbs. of chloracetic acid to 490 gals. of water, and the treatment of the resultant solution with 1,085 lbs. of soda ash with a final temperature for the resultant solution of 50°C , being obtained in order to assure completion of the conversion to sodium chloracetate.
2. The application of a 2-HP dual marine-propeller type mixer assembly to the contents of K1 during the dissolution of the chloracetic acid in water and the conversion of chloracetic acid to sodium chloracetate.

- 1 -
3. The use of approximately 19 sq.ft. of heat exchange surface in the form of an internal helically-wound coil for the raising of the temperature of the final solution to 50° C., during one hour, when 210° F. steam is employed as the heating medium.

The Continuous Preparation of Sodium Hydrosulfide

The system for the preparation of H₂S-saturated sodium hydrosulfide solution actually comprises:-

1. A unit for the continuous feeding of sodium hydroxide in proper concentration in aqueous solution to an absorption column.
2. An "absorption" unit for the contacting of the sodium hydroxide solution from (1) above with H₂S for the purpose of forming the sodium hydrosulfide and saturating a solution of the same with H₂S.
3. A unit for continuously generating the required H₂S to the demand rate of the system.
4. A system for "conditioning" (de-watering) the recycle saturated H₂S as reclaimed from the H₂S Flash System.

The sodium hydrosulfide is formed in such quantities as to be present in 10% excess over stoichiometric requirements for the reaction with the sodium chloroacetate. The pressure of H₂S over the system is 220 psig, at which pressure a saturating of the system to the extent of approximately 0.28 lbs. of H₂S (as H₂S in a state of dissolution in the sodium hydrosulfide solution) per pound of thio-glycolic acid produced finally is involved.

The preparation of sodium hydrosulfide solution, which is synonymous with the starting up of the plant, involves the throwing of the master switch, C16, (see wiring diagram for relay C2). Observing the wiring diagram, it will be apparent that the throwing of the master switch, C16, accomplishes the following:

1. Through a circuit from power supply to A⁺ through B⁺ to ground,
 - a. The pilot switch for the agitator on E12 is thrown into operation. This assures the best conditions for the rapid absorption by the material in E12 (the sump component of the H₂S Flash System) of

"steady-state" temperature during the plant start-up heating of this material.

- b. The air pilot, C21, atwart the pneumatic circuit from the temperature instrument, C37, to the controlled steam input valve, V13, is opened, thus applying heat to the material in K12, to provide for the achievement of "steady-state" temperature mentioned in (a) above.
 - c. The air pilot, C20, atwart the pneumatic control line from the flow instrument, C36, to the controlled valve, V11, is opened, providing for the assumption of "steady-state" conditions by the gas phase in the flash column, K11.
 - d. The air pilot, C28, controlling the pneumatic transmission from the temperature instrument, C11, on the condenser, K16 to the control valve, V23, is opened, providing for the condensing of water from the gaseous effluent sent from K11 to K16.
2. Upon assumption of steady-state temperature conditions in K12, as assured by the opening of the air pilot C21 and as detected by the temperature instrument C37 (the pneumatic signal from which is converted to an electrical signal through the pressure switch C22), with the assurance that water in appropriate amounts will be provided to the condenser K16 (through the opening of the air pilot C28), with the assurance that steam will be furnished in the appropriate rate of supply as controlled by the flow instrument C36 to the internal coil of the Flash Column (because of the opening of the pilot valve C20), with the assurance (through the contacts "F" of the relay C6 and the contacts "E" of the timer circuit C5) that all of the operations pertinent to the preparation of the requisite amount of sodium chloracetate has been accomplished, with the assurance (through the pressure switch C13) that an appropriate pressure of H_2S is available, with the assurance (through the pressure switch C11) that caustic soda solution is present in adequate supply, and with assurances that sulfuric acid is also present in adequate supply (through the pressure switch C26), the circuit from power supply through the holding coil of the relay C8 is completed. Through the power contacts of the relay C8, all members of the continuous product system are set into motion.

All conditions established by or upon the master switch C16 having been achieved, the relay C8 through its power contacts "H" proceeds to feed the sodium hydrosulfide solution stored in the sump E8 by means of the pump P4 to the reactor system. In consequence of this action, the float member of the level switch C11a dropped to a position such that the contacts of C11 through the pilot switch C90 set the pumps P2 and P3 into operation. P2 is a proportioning pump delivering the caustic soda solution at a prescribed rate, while the pump P3 delivers water at a rate such that a dilution of the caustic soda solution from its starting concentration of commercial 50% caustic soda solution to approximately 1.11 lbs.

per gallon of water is obtained. The combined streams are homogenized by being forced to pass through a series of orifice plates forming an orifice manifold mixer, K19, and proceed thence to the absorption column. Simultaneously, and at a rate such that a pressure of 220 psi of H_2S is maintained over the solution, H_2S (composed of reclaimed H_2S from the H_2S Flash System and newly generated H_2S from the H_2S Generator) is fed from the Compressor, K17, to the absorption column. The operation of the Compressor, K17, is controlled solely by the pressure output switch, C17, athwart the circuit of the pilot switch for the compressor drive as shown in the wiring diagram for K17, to maintain 220 psig. of H_2S pressure over the absorption system. The heats of reaction between the H_2S and sodium hydroxide and of solution of the excess H_2S in the sodium hydrosulfide solution are absorbed by the recycling of a stream of chilled, finished sodium hydrosulfide solution from the Sump, E8, by means of the Pump, P8, through the refrigerated cooler, E20, to the top of the column, E7. This amounts to the blending of a finished stream of sodium hydrosulfide solution (from which sensible heat in equivalent quantity to the combined heats of reaction and solution in E7 is abstracted in E20), with the influent NaOH solution feed. During the passage of the blended streams down through E7 which is a lead-lined column packed with berl saddles, the influent NaOH solution is converted to sodium hydrosulfide and is saturated with H_2S to equilibrium with 220 lbs. of H_2S pressure at 20° C.

For a plant with an output capacity of 30,000 lbs. per 8-hour day, 25-day month of thioglycolic acid, there are employed:

1. A 10-HP, two-stage compressor, representing K17;
2. A 45-inch diameter by 6'0" height column packed with $1\frac{1}{2}$ " berl saddles; representing E7;
3. Using 40° F. Freon as the refrigerant, a 167 sq.ft. heat exchange surface, uni-pass, "U"-tube type heat exchanger (representing E20) for the cooling of a 26 gpm recycle stream to the extent of 20° F. The refrigerant is handled on the tube-side of the lead-surfaced copper tubes while the aqueous product solution is handled on the shell-side of the exchanger.

In connection with the operation of the sodium hydrosulfide solution preparation system, there remains but to mention two pertinent factors:

1. H_2S gas is made available through the action of sulfuric acid on iron pyrites in an H_2S generator of conventional design.
2. In view of the facts that the corrosive action of wet H_2S represents a virtually insoluble problem from the standpoint of materials of construction for the compressor, K17, while dry H_2S represents no particular problem, a system comprising condensers K16 and K21, and the dryer, K22, is employed to assure that recycled, excess H_2S coming from the Flash System and the H_2S from the H_2S generator, K5, are thoroughly dried before delivery to the compressor, K17.

For a plant of the above stated capacity

1. Using an influent water temperature of $82^\circ F.$ and ΔT for the water stream of $40^\circ F.$, a uni-pass, "U"-tube type heat exchanger (representing K16) with approximately 80 sq.ft. of heat exchange surface establishing an effluent H_2S gas temperature of $100^\circ F.$ is employed; while a heat exchanger of the same basic construction by having 41 sq.ft. of heat exchange surface serves the purpose of K21, using $40^\circ F.$ feed as an effluent product temperature of $50^\circ F.$
2. The dryer component (K22) of the system is of the activated alumina adsorption and regenerative type, and of conventional design. The function of the heat exchange bank is to reduce the mol fraction of water as a vapor of saturation in the H_2S gas to economic limits with respect to water and refrigeration costs, as well as with respect to the initial cost and cost-of-operation of the dryer equipment.

The Production of Sodium Thioglycolate

As previously observed, the preparation of the sodium hydrosulfide solution containing an excess of H_2S is a continuous operation which is carried out as one continuous operation in the company of the continuous operations to form sodium thioglycolate and to convert sodium thioglycolate to crude thioglycolic acid. Assuming therefore that the conditions established by and upon the master switch circuit have been satisfied, the agitator components of the Reactors K9 and K10 are set into operation through the closing of the contacts "Q" and "R" of the relay C3. Furthermore, the pump P4 feeding the sodium hydrosulfide solution and the pump P1 feeding the sodium chloroacetate solution, through the closing of the power

contacts "D" of C8, are set into motion. The streams from E8 and K1 representing the sodium hydrosulfide solution and the sodium chloracetate solution, respectively, are fed into a bank of reactors formed by E9 and K10. E9 consists of a heavy-walled, lead-lined tube capped at both ends, with a length-to-diameter ratio of approximately 6:1 down through the principle axis of which there passes, through a high-pressure stuffing box in one end of the tube's capped ends, an agitator shaft on which a multiplicity of equi-spaced paddle blades are mounted. The blades apply a rotation couple to the mass in the reactor against the braking action provided by a set of baffle fins attached to the internal wall of the reactor tube and running the entire length of the tube.

The combined effects of the feeding of the sodium chloracetate solution at 50° C. and the heat-of-reaction engendered in the reaction between the sodium hydrosulfide solution and the sodium chloracetate will, under moderate conditions of insulation of the reactor, E9, against loss of heat by radiation and convection, insure an effluent reaction stream temperature of approximately 94° F. The use of the 6:1 ratio of length to diameter for the reactor and the use of agitation by the application of a simple rotation couple by paddle blades (with no propelling component in or against the direction of mass flow) provides for a minimizing of end-to-end blending of the reactors' contents and hence a maximum simulation of a simple displacement type of flow through the reactor.

In providing for a displacement type of flow as opposed to a homogenizing of the contents of the reaction stream, the hold-up time within the reactor, E9, is minimized since the effects of dilution of the influent streams by the highly-reacted material at the discharge end of the tube is avoided. The reactor, K10, is identical in construction with E9, except for the fact that the cylindrical portion of the reactor is jacketed for the application of steam heating of the vessel's contents. Through the heating of the reactor, K10, by way of the jacketed

surface of the vessel as previously mentioned, an effluent reaction stream temperature of 115° F. is obtained.

The conditions of design for K9 provide for an average retention time within that reactor of ten minutes, while the conditions of design of K10 provide for a retention time within that unit of approximately three minutes. The bulk of the reaction takes place in reactor K9 with reactor K10 serving as the point at which advantage is taken of the increase in the reaction velocity coefficient for the reaction resulting from the application of higher temperatures, thus assuring the quickest possible completion of the reaction against the normally retarding factor of dilution of the reaction streams. The conversion to sodium thioglycolate is, at this point, approximately 97% of theoretical, based on the amount of chloracetic acid employed.

The Conversion of Sodium Chloracetate to Crude Thioglycolic Acid

The effluent stream from the reactor K10 passes to K11 through the valve, V12, which is regulated by the pressure instrument, C13, to maintain a constant back-pressure on the previous portion of the system. Since the pressure over the system in the H_2S Flash Column, K11, is maintained at slightly above atmospheric, the passage of the reaction stream across the valve V12 involves the flashing of the bulk of the excess H_2S . That portion of the H_2S which is immediately relieved on the down-stream side of valve V12 enters the foam separator, K13, where a separation of the gas and the vapors-of-saturation contained therein from entrained liquid is effected, the liquid returning to the line by which it flows into the unit K11. The immediate zone, the "free" zone, in the column K13 into which the line down-stream from valve V12 enters is an empty space bounded at the upper end by a perforated plate supporting a two-foot height of berl saddles, and bounded at the lower end by the top surface of a column of randomly-packed berl saddles stretching from the bottom of the column to a point as equi-distant from the point of entry into the column as the above-mentioned perforated plate. This "free zone"

acts as a disengagement space for the two-phase stream which enters K11. Into the packed zone above the free zone there is effected a constant rate feed of 69% sulfuric acid in quantities slightly in excess of that required to react with the excess sodium hydrosulfide solution, and sufficient to convert the sodium thioglycolic acid content of the entering stream to thioglycolic acid. The combined effects of the low solubility of H_2S in an acidic stream along with the application of heat through an internal coil located in the packed zone beneath the free zone is sufficient to secure an elimination to negligible dimensions of excess H_2S from the effluent crude thioglycolic acid stream.

The mixing of the sulfuric acid with the influent sodium thioglycolate stream is accomplished principally in the packed zone beneath the free zone. The liquid effluent from the H_2S flash column will, under proper design conditions, have a concentration of 1.225 lbs. of thioglycolic acid per gallon of solution, and will contain sodium chloride, sodium sulfate, excess sulfuric acid as its main impurities as well as chloracetic acid and dithioglycolic acid as trace impurities. This liquid effluent passes from the flash column to the sump, K12, where it is maintained at a temperature of $170^{\circ} F.$, through the action of the temperature instrument, C37, controlling the input of steam by way of control valve V13 to the internal coil in K12. The intermittent exhausting of the contents of K12 to the crude thioglycolic acid storage K15 is effected by the level control instrument, C23, which is identical in its principle mode of operation with that of the level instrument, C3. The intermittent "pumping-down" of the contents of K12 to the minimum level controlled by the instrument C23 is effected through the delivery of the signal from C23 to the pilot switch C24 in the circuit of the drive for the pump P5 and through the simultaneous delivery of the signal from C23 to the valve V4 as set forth in the wiring diagram for K12. The effluent H_2S from the Flash Column K11 and the Foam Separator K13 are joined up and passed to the condenser and dryer system on the up-stream side of the Compressor K17 for the purpose previously described, prior to the recharging of the absorption column K7 with the

the recycled H_2S by the compressor K17. The recycled H_2S is joined with fresh H_2S from the H_2S generator at the inlet point of the condenser, K16. Control over the rate of H_2S make-up by the H_2S generator, K5, is by way of the pressure instrument C12. The flow of refrigerant fluid to the condenser K21 receives its starting impulse from the closing of contacts "S" in the relay C8, after which the temperature instrument C19 measuring the temperature of the effluent gas from K21 becomes the conditioning factor.

For the plant capacity named above, the Flash Column is $1\frac{1}{2}$ ft. in diameter, is packed with 1" berl saddles to a height of 10 ft. beneath the "free zone", has an overall "free zone" height of approximately $\frac{1}{2}$ ft., and a packed zone above the "free zone" of 2 ft. The sump component of the system is furnished by an 18 in. diameter x 24 in. straight-side chamber which is provided with ten turns of 1 in. lead-coil on a 12 in. mean diameter. Both the Flash Column and the sump are of lead-lined construction.

THE PRICE ART

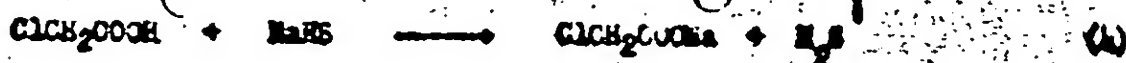
Thioglycolic acid is generally prepared commercially by the reaction of chloroacetic acid with thiourea to form a thiouronium complex which is then decomposed by heating with an alkali to sodium thioglycolate, after which the sodium thioglycolate is converted to thioglycolic acid by treatment with a mineral acid. This process suffers from several disadvantages of which one of the greatest is the high cost of thiourea. This disadvantage is aggravated by the fact that 44 parts by weight of the thiourea is converted to cyanamide and other irrecoverable products for every 32 parts by weight which appears in the finished product. That is to say, the only part of the thiourea molecule, $(NH_2)_2CS$, which appears in the thioglycolic acid is the sulfur atom.

In spite of the disadvantages of the thiourea method, the alternative method of reacting sodium hydrosulfide with chloroacetic acid has not been used industrially because it has had even more serious shortcomings.

Klason and Carlson (Ber., 32, 732 (1906)) prepared thioglycolic acid by adding a solution of chloroacetic acid to a 15% potassium hydrosulfide solution containing 2 moles of hydrosulfide. The second mole of hydrosulfide is required to convert the chloroacetic acid to its potassium salt. Klason and Carlson state that the chloroacetic acid can first be neutralized with alkali and the solution of the salt added to one mole of potassium hydrosulfide. In small trial experiments they claim they obtained yields ranging from 57.7% using 50% potassium hydrosulfide and 0 parts water per part of chloroacetic acid to 99.6% using 15% potassium hydrosulfide solution and 7 parts of water per part of chloroacetic acid. They state, therefore, that higher dilutions favor increased yields. The yields they describe seem to be greatly exaggerated (see examples 1 and 2, which are appended hereto as illustrative of the general technique used by Klason and Carlson). A possible source of error (the method of determining the yield is not stated) is the determination of hydrogen sulfide as thioglycolic acid, the amount of dissolved hydrogen sulfide increasing with the amount of water, and the apparent yield therefore increasing with dilution of the reaction mixture.

Schütz (Angew. Chemie, 46, 780-1 (1933)) claimed a 99% yield of pure thioglycolic acid by adding an aqueous solution of chloroacetic acid to a solution of sodium hydrosulfide saturated with hydrogen sulfide. Previous investigators had obtained very poor results by this method. Schütz attributed his high yield to the use of sodium hydrosulfide which had been freshly prepared by passing hydrogen sulfide into sodium hydroxide solution. He stated that the sodium hydrosulfide of commerce had deteriorated so much because of atmospheric oxidation that it was unsuitable for the preparation of thioglycolic acid in high yield. Among the claims made by Schütz is the claim that no hydrogen sulfide is evolved during the addition of the chloroacetic acid solution to the hydrosulfide solution. This is a very unexpected result since the addition of a comparatively strong non-volatile acid such as chloroacetic acid to a solution of a salt of a weak, volatile acid such as hydrogen sulfide should result in the evolution of gas according to the following:-

15



In fact, we have found, on repeating the procedure described by Schütz, that a vigorous evolution of gas takes place throughout the addition of the chloroacetic acid. Furthermore, we have found that the yield of thioglycolic acid obtained by this procedure is actually in the neighborhood of 20% instead of 99% as claimed by Schütz.

Because of the extremely poor yields obtained in the past by the sodium hydrosulfide method and because of the inconvenience associated with its use, it has not been used for the commercial preparation of thioglycolic acid in spite of the low cost of the starting materials and the directness of the method. By our invention we have succeeded in eliminating the objections to the method.

The claims of Schütz are manifestly absurd in view of his statement that no evolution of H_2S was observed upon contacting freshly-prepared sodium hydrosulfide solution with chloroacetic acid. In view of the relative magnitudes of the ionization constant of chloroacetic acid (namely 1.5×10^{-3}) and much lower dissociation constant for H_2S (9.1×10^{-8} for the first ionization — $\text{H}_2\text{S} \rightleftharpoons \text{HS}^- + \text{H}^+$; and 1.2×10^{-15} for the second ionization — $\text{HS}^- \rightleftharpoons \text{S}^{2-} + \text{H}^+$) and the limited solubility of H_2S in salt solution, Schütz' specific constant in this direction brands the whole character of his work, since by all the laws of physical chemistry the reaction



could have no other basis for shifting in the left-hand direction than that the above-stated relative magnitudes of dissociation be of reverse order.

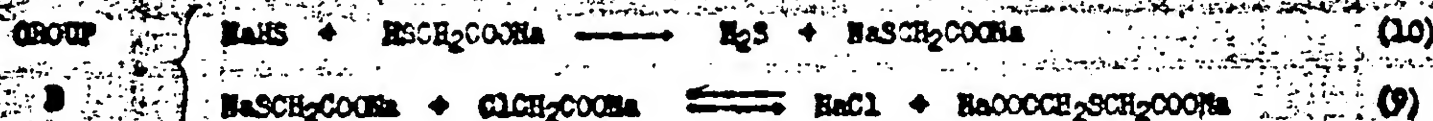
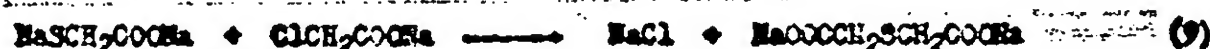
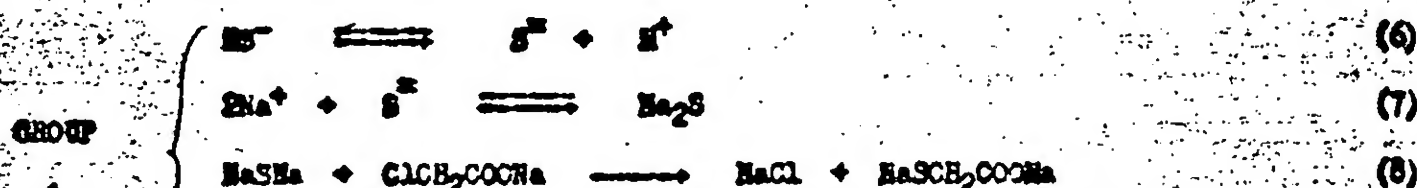
The work of Klason and Carlson, at least superficially, is of a higher order than that of Schütz and shall be so treated below in connection with our statement of claims.

THE CLAIMS

The route of our invention lies separately in the novelty of the engineering features and the novelty of certain aspects of the chemistry, as well as in the intertwining of the chemical and the engineering features of the invention. These points of novelty are:

1. Operation under a "super-atmospheric pressure of H_2S

The replacement of chlorine by a sulfhydryl group to form thioglycolic acid from chloroacetic acid differs from the conventional mercaptan synthesis from alkyl halides in that a chlorine atom in the alpha-position to a carboxyl group shows a greatly enhanced reactivity. This enhanced reactivity increases the possibility of side reactions. It is therefore generally conceded that the principal deterrent to high yields of thioglycolic acid by the hydrosulfide-chloroacetate salt technique lies in the side-reactions to produce dithioglycolic acid as per the following:



and the variants thereon. With respect to Equation (6) which is basic to the production of $NaSCH_2COONa$ via Equation (8), it is apparent that the excess of H_2S present in our system in consequence of the "super-atmospheric" pressures of H_2S employed by us in preparing the $NaSH$ solution produces the contending phenomenon to (6), namely: $S^{2-} + H_2S \rightleftharpoons 2HS^-$. Similarly, in Equation (10) which is basic to the second-named means of forming $NaSCH_2COONa$, we find, by viewing

the right-hand side of (10), that the excess of H_2S would displace the reaction in the opposite direction. Thus the two paths of approach to the formation of $NaSCH_2COONa$, and hence to the formation of the ether compound side-reaction product, are effectively blocked by the use of the large excess of H_2S in the system.

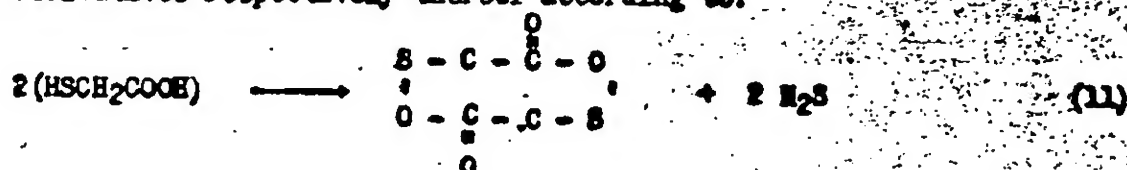
At this point, we do well to mention the work of Klason and Carlson. The validity of the mechanisms proposed in Equations (8) and (10) are too well based on the distinguished acidity of the hydrogen atom of the sulphydryl to warrant contradiction. Moreover, the relative irreversibility and existence of the reaction in Equation (9) is not open to question. Hence, the existence of the ether-forming side-reaction as the principle side reaction is beyond doubt. Klason and Carlson stated that the great dilution of their system, for a 97.6% yield, favored the hydrolysis of the $NaSCH_2COONa$ to $HSCH_2COONa$, thereby defeating the reaction according to (9). It is self-evident that this is possible. But it is important to observe that this takes place at a tremendous sacrifice in dilution of his final solution with respect to the thioglycolic acid. This would mean a concentration of acid, prior to treatment of the sodium thioglycolate with acid of 0.51 lbs. of thioglycolic acid per gallon of final solution. Since the final product must be isolated by extraction from aqueous solution and distillation (if desired in pure acid form) or extraction from aqueous solution with an organic solvent plus a subsequent extraction of the organic solution by an aqueous alkaline solution (if desired in its pure salt form) it is apparent that the isolation of the final product from the original crude is a much more difficult task than in our case where we produce a far more concentrated crude. This is especially true in view of the extreme solubility of thioglycolic acid in water, and the consequent poor distribution coefficient between the extracting organic solvent and the crude aqueous solution.

2. The Use of a Continuous Mode of Manufacture

Granting, as demonstrated above, the desirability of employing a sodium hydrosulfide solution which is surcharged with excess H_2S to the maximum possible

extent, the greater the excess of H_2S (and greater concentration than that given for the illustrative plant would be desirable^{3/}) present the more logical does the continuous method of manufacture become. The conclusion arises from:-

1. The fact that in any case production of thioglycolic acid involves a dilute system with respect to the thioglycolic acid content of the final crude solution. The manufacture of thioglycolic acid in highly concentrated crude solutions risks the formation of lactide and polymeric derivatives respectively thereof according to:



While it is true that such lactides and polycondensation products would be susceptible to saponification, the act of saponification would of itself involve a dilution of the final product.

The batch execution of the above-mentioned process requires an unusually large, and therefore extremely expensive, autoclave for the magnitude of pressure involved. Despite the short reaction time required, a decision to employ a multiplicity of batches per day to reduce the size of clave needed would run afoul of the fact that the relieving of the mass of its excess H_2S would, for a short cycle of relief, involve tremendously large absorption equipment; or, for an extended cycle of relief, would impose a long "dead cycle" (with respect to the actual task of the vessel-- which is reacting). A decision to circumvent these objections by passing the reacted mass to a storage point from which it would be doled out to the H_2S flashing equipment, would build up the amount of expensive pressure vessel equipment involved in the plant.

2. From the number of controls applied to the continuous plant as shown on the accompanying flowsheet, it is apparent that there exists a multiplicity of opportunities for failing to impose optimum conditions upon the process. These disastrous opportunities arise from the nature of the chemistry involved, which is complicated, and is therefore implicit in the chemistry rather than in the plant design.

The enlarged opportunities for instrumenting continuous type plants for the maintenance of steady-state, and therefore, constantly-held conditions as compared with the ability to impose automatic control on the variable conditions involved in batch-type operation, argue again in favor of the use of continuous type production and is related to the nature of the chemistry involved. Furthermore, in connection with the subject of in-

^{3/} Patent protection for operation in liquid H_2S as a solvent material, exclusive of the water entering the system with the sodium chloracetate solution, and for a system involving a reaction between molten sodium chloracetate and H_2S in liquid H_2S should also be requested.

strumentation, the enlarged opportunities for instrumentation of a continuous type plant mentioned above also mean that an enormous savings in manpower per unit of production can be effected, thereby minimizing the cost of production of this material.

It is important to observe that while in the plant which we have designed, a failure at any one point means the discontinuation of operation of the entire plant, thus eliminating the possibilities of "carrying the error" from one point to another, a failure at any point in the operation of a batch-type system would involve the carrying of that failure to its ultimate conclusion to the rest of the processing sequence.

The effect of continuous-type production (with its susceptibility to constant and automatic control) on uniformity of end product from day to day is almost too obvious to warrant further discussion.

3. In addition to the general economy involved in smoothly spreading surge loads, with respect to both chemical and chemical thermodynamic inertias, such as are involved in a process of this type over a period of time and thereby enabling the use of smaller size equipment for each of the individualized tasks, there exists the added consideration that the continuous process lends itself unusually well to the exclusion of air from the system which, in the case of thioglycolic acid, would involve a deterioration of the end product if the exclusion of air were not provided for. Again, in view of the excess of H_2S employed by the process and the consequent necessity for relieving the same from the system at the end of the process, the continuous production method, with its constant and equalized trading between units carrying out individualized tasks permits of the easy recycling of the excess H_2S without, at any point, necessitating venting to the atmosphere of this material even when shutdown operations are involved.

ADDITIONAL CONSIDERATIONS

It might also be well to attempt to get protection on the system of ideas involving the following:

1. A reaction between molten sodium chloracetate and sodium hydrosulfide in liquid H_2S solution, in which a far more concentrated end product resulting in the formation of the polymeric and lactide forms of thioglycolic acid are the end products of the reaction.
2. A subsequent operation in which the polymeric and lactide end products are saponified with ammonia hydroxide, sodium hydroxide, calcium hydroxide or any other alkaline aqueous medium to produce the salts of thioglycolic acid.

EXAMPLES

1. Reaction under atmospheric pressure: A solution of 42.5 g. sodium hydroxide in 350 cc. water was saturated with hydrogen sulfide at 21° C. A solution of sodium chloracetate prepared by dissolving 95 g. chloracetic acid in 200 cc. water and adding 53 g. sodium carbonate was added slowly with the temperature being kept below 28° C. by cooling. After all the sodium chloracetate solution had been added, the reaction mixture was warmed to 95° C. during a period of one-half hour and slowly cooled to room temperature. Titration of a sample after acidifying with sulfuric acid indicated a 60% yield of thio-glycolic acid.

2. A solution of 22 g. sodium hydroxide in 150 cc. water was saturated with hydrogen sulfide at 5° C., while cooling in an ice bath. To the sodium hydrosulfide solution thus prepared there was added a solution of sodium chloracetate prepared by dissolving 47.5 g. chloracetic acid in 100 cc. water and adding 26.5 g. sodium carbonate. The temperature of the reaction mixture was kept at or below 5° C. during the addition and a slow stream of hydrogen sulfide was passed through. After standing at 5° C. for two hours the reaction mixture was warmed to 50° C. for one-half hour. Titration of a sample indicated a yield of 61.5%.

65-4307
420

SAC, Philadelphia

7/10/50

SA T. SCOTT MILLER

HARRY GOLD, was.
ESPIONAGE - R

EXHIBIT 65-4307-1B-13 (9) (Exhibit 20)

On 6/22/50, GOLD examined this material, at which time he stated that the notes dated in November of 1946 were in his handwriting and were concerned with literature work in the library by GOLD on the oxidation of dimethyl hexane diol, which process the BROTHMAN firm was working on.

GOLD stated that the material in the tablet is in his handwriting and is concerned with the diol process above.

The notes dated 11/20/47 are in GOLD's handwriting and are literature searches on a formula for the decomposition of acetate and relate to a projected process for the production of methyl alcohol. This was done for the BROTHMAN firm by a man in Brooklyn.

The single sheet of paper dated 11/2/47 was work in connection with the process for making a high test bleach for the METTUR CHEMICAL COMPANY of India.

The letter dated 12/3/47 was merely in connection with business of the BROTHMAN firm.

GOLD was unable to identify the notes on the small piece of yellow paper but stated that the notes were in his handwriting.

TSM:HKF
65-4307

THE GIRDLER CORPORATION

INCORPORATED

P. O. BOX 987

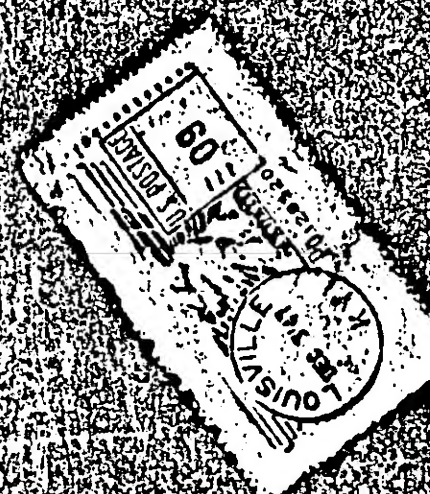
LOUISVILLE 1, KENTUCKY

THE **GIRDLER** CORPORATION

224 E. Broadway Louisville 1, Kentucky

A. Brothman and Associates
Chemical and Mechanical Engineers
85-03 — 57 Avenue,
Elmhurst, L. I.

Attention: Mr. A. Brothman, Chief Engineer.



110 02

3-5-49
miller ☒ P. 194

sol. 0.5 in 1/4 in 1/4 in @ 15% 2 at 1.2.

1 dy dists not more valuable.

0.2 value → 0.5 at 0.02

—————

3-5-48

O₅O₄

Ref. Mellor

XV

p. 707

Prep.

1. Heat finely divided Os in air at 400°C
2. O₅O₂, O₅O₃ and O₅O₄ readily go to O₅O₄ (volatile) on heating in air.
3. Heat a soln of K osmate → volatile O₅O₄

Reaction Behavior

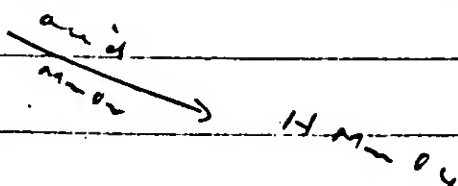
1. O₅O₄ acts to influence rate of decomposition of alkali chlorates. But M. says it is due to the formation of an additive compd. (gives 3 reasons)
2. O₅O₄ soluble 0.47 gm in 1 ml H₂O at 18°C
O₅O₄ soluble 2.50 gm in 1 ml CCl₄ (but solubility in H₂O decreases on addition of alcohol)

MnSO₄

n.g.

Mn(SO₄)₂

Mellor XII



Mellor XII p. 153

Mn and salts not influenced by atoms O

